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ÚSTAV CHEMIE MATERIÁLŮ

EFFECT OF ETHYLENE AND PROPYLENE ON PERFORMANCE OF ZIEGLER - NATTA CATALYST IN STOPPED - FLOW POLYMERIZATION

EFFECT OF ETHYLENE AND PROPYLENE ON PERFORMANCE OF ZIEGLER - NATTA CATALYST IN STOPPED - FLOW POLYMERIZATION

DOCTORAL THESIS
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AUTHOR AUTOR PRÁCE	Ing. Adam Hoza
SUPERVISOR ŠKOLITEL	Ing. Jan Kratochvíla, CSc.

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Zadání dizertační práce

Ústav: Ústav chemie materiálů
Student: **Ing. Adam Hoza**
Studijní program: Makromolekulární chemie
Studijní obor: Chemie makromolekulárních materiálů
Vedoucí práce: **Ing. Jan Kratochvíla, CSc.**
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Název dizertační práce:

Effect of Ethylene and Propylene on Performance of Ziegler – Natta Catalyst in Stopped – Flow Polymerization

Zadání dizertační práce:

Cílem práce bude příprava a charakterizace nových typů materiálů na bázi blokových kopolymerů technikou“ stopped–flow“. K tomuto účelu bude zkonstruována experimentální aparatura umožňující technikou“ stopped–flow“ syntézu dostatečného množství materiálu pro cílenou modifikaci vybraného komerčního sekvenčního kopolymeru polypropylenu.

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Ing. Adam Hoza
student(ka)

Ing. Jan Kratochvíla, CSc.
vedoucí práce

prof. RNDr. Josef Jančář, CSc.
vedoucí ústavu

V Brně dne 1.9.2016

prof. Ing. Martin Weiter, Ph.D.
děkan

Fakulta chemická, Vysoké učení technické v Brně / Purkyňova 464/118 / 612 00 / Brno

ABSTRAKT

Výzkum v této práci byl zaměřen na přípravu a charakterizaci blokových kopolymerů typu polypropylen-*blok*-poly(propylenu-co-ethylenu) (dále jen PP-*blok*-EPR). Tyto materiály jsou považovány za účinné kompatibilizátory mezi semi-krystalickou polypropylenovou (PP) matricí a amorfními doménami statistického kopolymeru propylenu a etylenu (EPR) v rázuvzdorném sekvenčním kopolymeru (ICP) a proto byl výzkum zaměřen na zkoumání vlivu přídavku blokového kopolymeru PP-blok-EPR na vlastnosti komerčního ICP. Blokové kopolymery byly připraveny za použití techniky „stopped-flow“. Pro tento účel byla zkonstruována vysokotlaká polymerační „stopped-flow“ aparatura, která umožňuje syntézu kopolymerů PP-*blok*-EPR za podmínek blízkých podmínkám v průmyslových reaktorech pro výrobu komerčních ICP materiálů. Aparatura umožňuje vyrábět PP-*blok*-EPR polymer v množství dostačující na jeho charakterizaci a následnou přípravu směsí s komerčním ICP. Velmi krátké polymerační časy (obvykle kolem 0.2 s) kterých bylo dosaženo v kapilárním reaktoru aparatury „stopped-flow“ zajišťuje, že aktivní centra Ziglorova-Nattova katalyzátoru produkují polymer řetězce skládající se z bloku semikrystalického polypropylenu a bloku amorfního EPR kopolymeru. Takovéto molekuly jsou v literatuře popsány jako „skutečné blokové kopolymery PP-blok-EPR“.

Kopolymery syntetizované v aparatuře „stopped-flow“ byly frakcionovány preparativní TREF (Temperature Rising Elution Fractionation) metodou a získané frakce byly následně analyzovány pomocí DSC, ^{13}C-NMR a GPC/SEC. Tyto analýzy odhalily přítomnost amorfního EPR ve vysoce krystalické frakci (100-140 °C). Toto zjištění potvrdilo, že významná část polymerních řetězců, připravených v aparatuře „stopped-flow“ jsou blokové kopolymery skládající se z bloku semikrystalického PP homopolymeru a bloku amorfního EPR kopolymeru v jednom polymerním řetězci.

Kopolymery získané metodou „stopped-flow byly v tavenině smíchány s komerčním rázuvdorným kopolymerem ICP. U takto připravených směsí byly vyhodnoceny mechanické vlastnosti, DTMA a reologické vlastnosti a výsledky byly srovnány s vlastmi původního komerčního ICP kopolymeru. Dále byly studovány rozdíly v morfologii a umístění EPR domén v matrici PP prostřednictvím SEM.

Zřetelný vliv kopolymeru PP-blok-EPR na vlastnosti ICP byl pozorován zejména v morfologických změnách EPR domén dispergovaných v PP matrici. Tyto změny mají pozitivní vliv na rovnováhu mezi modulem v ohybu a rázovou pevností ICP materiálu. Vliv kopolymeru PP-blok-EPR na reologické vlastnosti ICP byl nevýznamný. Podobně také v případě DTMA nebyl pozorován významný vliv kopolymeru PP-blok-EPR na vlastnosti ICP.

KLÍČOVÁ SLOVA

Stopped-flow, blokový kopolymer, polypropylén

ABSTRACT

The research presented in this thesis focused on the preparation and characterization of polypropylene-block-poly(propylene-co-ethylene) (hereinafter referred to also as PP-block-EPR). These materials are considered to be efficient compatibilizers between a semi-crystalline polypropylene (PP) matrix and amorphous ethylene/propylene rubber (EPR) domains in impact-resistant polypropylene copolymers (ICP). The effect of prepared PP-block-EPR copolymers on properties of commercial ICP materials was investigated. The unique PP-block-EPR copolymers were prepared by using the “stopped-flow” technique. For this purpose a high-pressure “stopped-flow” polymerization apparatus was constructed. This apparatus allowed the synthesis of PP-block-EPR copolymers under conditions comparable to conditions applied in industrial reactors for the production of standard ICP materials. The apparatus also enabled the production of sufficient amounts of materials for characterizing and subsequent blending with ICP. Very short polymerization times (typically around 0.2 s) applied in “stopped-flow” capillary reactors ensured that the active sites of a Ziegler-Natta catalyst produced polymer chains consisting of a block of semi-crystalline polypropylene (PP) and a block of amorphous ethylene/propylene random copolymer (EPR). Such macromolecules are described in the literature as real PP-block-EPR copolymers.

Copolymer materials synthesized in the “stopped-flow” apparatus were fractionated by the preparative means of Temperature Rising Elution Fractionation (TREF). The fractions obtained were subsequently analysed by DSC, ^{13}C-NMR and GPC/SEC methods. These analyses revealed the presence of EPR, also in a crystalline fraction (100 – 140 °C). This finding confirmed that a noticeable portion of polymer chains, produced in the “stopped-flow” polymerization, were real block copolymers consisting of semi-crystalline PP homopolymer and amorphous EPR copolymer in one polymer chain.

The prepared samples were blended in melt with a commercial ICP material. Tensile properties, DTMA and oscillation rheology were evaluated on the prepared blends and the results compared with the properties of the original ICP copolymer. Furthermore, the differences in EPR domain morphology and location in the PP matrix were studied by SEM.

The obvious influence of the PP-block-EPR copolymer on ICP properties was observed mainly in morphological changes of the EPR domains dispersed in the PP matrix. These changes showed a positive influence on the balance between the flexural modulus and the impact strength of ICP material. The influence of the PP-block-EPR copolymer on ICP rheology was insignificant. Similarly, also in the case of DTMA no obvious influence of PP-block-EPR copolymer on the dynamic-mechanical properties of ICP was observed.

KEYWORDS

Stopped-Flow, block copolymer, polypropylene

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....
podpis studenta

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CONTENTS

1 INTRODUCTION

1.1 STOPPED-FLOW TECHNIQUE FOR 1-ALKENE POLYMERIZATION

In a conventional process of propylene or ethylene polymerization with a $MgCl_2$-supported Ziegler-Natta catalyst, the polymerization is usually performed for 1 – 3 hours during which the polymerization rate varies. The change, typically a decrease, in polymerization rate over time is caused by various chain-transfer reactions together with changing the active sites performance [1].

Conversely stopped-flow polymerization is conducted within an extremely short time period (tenths of second). The most predominant feature of the stopped-flow technique is its quasi-living polymerization characteristic. The polymerization time in the stopped-flow apparatus is shorter than the average lifetime of the growing polymer chain, which ensures that the states of active sites are not significantly influenced by time-dependent changes and chain-transfer reactions [2, 3].

One of the most attractive features of this method is the ability to obtain the polymer produced in the initial polymerization stage, which directly reflects the nature of the active sites just after their formation. Accordingly, the method was found to be useful for the study of the nature of the active sites, as well as for the assessment of their kinetic parameters [4, 5].

Characteristics such as the constant polymerization rate and negligible chain-transfer reactions within an extremely short period of time cannot be achieved by any other polymerization technique used for investigation of Ziegler-Natta catalysts [2].

The stopped-flow technique has been proven to be a powerful tool for elucidating kinetic mechanisms and polymer particle morphology [1, 5]. Keii and Terano were the first who utilized the stopped-flow method to follow the kinetics of propylene polymerization with an $MgCl_2$-supported Ziegler–Natta catalyst, in 1987 [6]. This technique was originally developed by Chance in the early forties for studying fast enzyme reactions [7].

In its basic form a principle of stopped-flow technique is as follow: Two reagents are driven through tubes to come into contact, then the reagents flow mixed together for a certain time into a flask containing a quenching agent. In order to be able to utilize the stopped-flow technique, it is necessary to meet the following requirements [2]:

- The active sites on the catalyst have to be formed by interaction with the co-catalyst instantaneously. Thus perfect mixing of catalyst and co-catalyst is required.
- The time required for the formation of the active sites at the beginning of the polymerization must be negligible compared with the polymerization time.

- Stirring of the catalyst slurry in the vessel should be efficient in order to avoid temperature and concentration gradients.
- During polymerization the flow velocity has to be constant.
- Monomer conversion has to be kept below ca. 10 % so as to be able to ignore the changes in monomer concentration and polymerization temperature.
- Polymerization has to be terminated immediately and completely after the reaction in order to avoid deviations in polymerization time and to be able to ignore the unfavourable side reactions induced by slow and/or reversible termination reactions.
- A sufficient amount of polymer has to be obtained to perform all the required analytical measurements.

1.1.1 Stopped-Flow Polymerization Apparatus

The basic stopped-flow polymerization system with two vessels has been extensively applied to study the homopolymerization and non-block-type copolymerization of olefins. A schematic drawing of the stopped-flow apparatus is shown in Figure 1 A. In the case of a typical polymerization procedure, the catalyst slurry and the co-catalyst solution, both saturated with monomer, flow simultaneously through a Teflon tube from vessels A and B into flask C containing a quenching agent. Polymerization is running in the PTFE tube from point X to point Y, and then the reaction is terminated in the quenching vessel. The time of polymerization can be adjusted by changing the length of the polymerization tube or by changing the flow rate of catalyst components [2, 3, 8, 9].

One of the most important features of the stopped-flow technique, quasi-living polymerization, can be utilized to synthesize olefin block copolymers with well-defined structures [2]. Research on catalyst pre-treatment within a very short period and synthesis of special block copolymers is performed using a three-vessel stopped-flow apparatus, which is schematically illustrated in Figure 1 B. Here, the catalyst slurry and the co-catalyst solution with propylene are placed in vessels A and B, respectively. The solution saturated with ethylene is in vessel C. The polymerization of propylene proceeds in the Teflon tube between points X and Y, then the subsequent copolymerization of propylene with ethylene takes place between points Y and Z. At point Z the polymerization is terminated [2, 8].

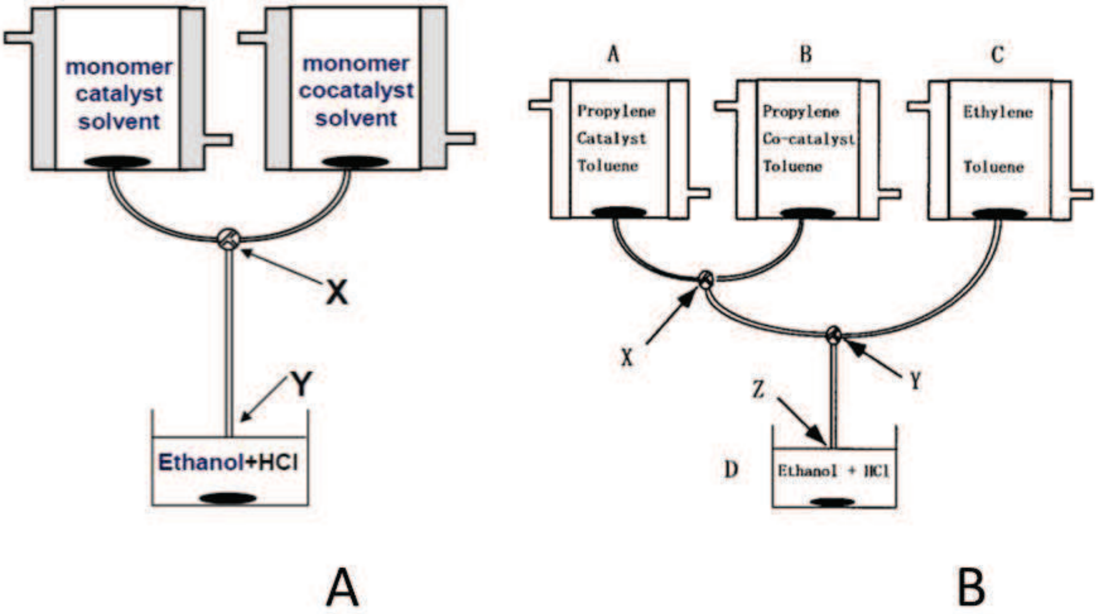

Figure 1: Schematic illustration of Stopped-Flow polymerization apparatus for homopolymerization (part A) and synthesis of block copolymers (part B) [2].

1.2 BLOCK COPOLYMER

The impact resistant copolymer of propylene and ethylene is sometimes called a “block-type copolymer”, but actually it does not have a true block-type structure, because the lifetime of the growing polymer chain is extremely short compared with the residence time in industrial polymerization reactors.

As mentioned in Chapter 1.1, the stopped-flow technique can be utilized for the synthesis of real olefin block copolymers. As was mentioned above this cannot be accomplished by the traditional sequential polymerization process, even on laboratory scale [2].

Real block copolymers (BCP) are composed of two or more chemically distinct blocks of polymers, which are covalently bound together [10, 11, 12, 13] in a single macromolecule. The simplest architecture is the linear AB-diblock copolymer, in which a polymer chain of type A monomers is covalently linked to a polymer chain of type B monomers. The linear AB-diblock copolymer is usually prepared by the repeated addition of monomers of B to the end of a previously synthesized chain of homopolymer A [14].

1.2.1 High impact resistant polypropylene copolymer

It is known that commercial high impact resistant copolymer polypropylene (ICP) produced by a multistage polymerization process forms a multiphase system as shown in Figure 2 [15, 16, 17, 18, 19, 20, 21, 22, 23, 24]. Isotactic polypropylene (iPP) and ethylene-propylene rubbers (EPR) are generally incompatible and their mixtures are thus heterogeneous. Phenomena such segregation, stratification and phase inversion could be therefore expected similarly as in other multiphase polymer systems [4].

It was observed that when iPP and EPR components are mixed only mechanically, the dispersion of the copolymer phase is not uniform and the desired mechanical properties are not achieved [25].

The first impact copolymer polypropylene (ICP), a designation commonly used for the “*in-situ*” blend of iPP and EPR, made directly during the polymerization, was prepared by the Montell Company in 1960 [26]. They found that “*in-situ*” blends apparently exhibited better properties than similar blends prepared by simple mechanical mixing of iPP and EPR components.

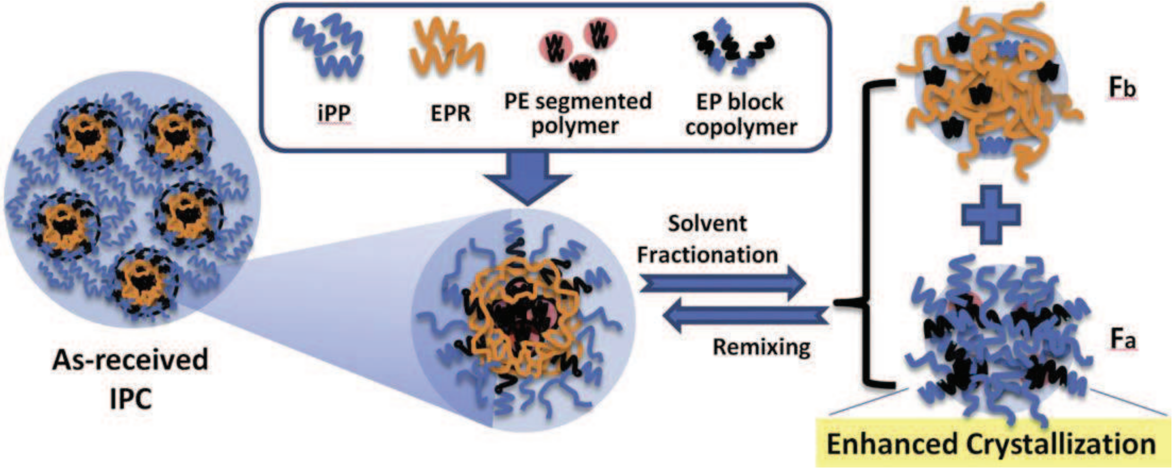

Figure 2: Schematic model depicting the relationship between phase structure and crystallization behaviour in ICP. (F_a is the xylene insoluble fraction and F_b is the xylene soluble fraction) [24].

Lot of studies have focused on the investigation of the influence of EbP diblock copolymers on the properties of ICP [15, 27, 17, 18, 29, 24, 30, 31, 32, 33]. It is known that during crystallization of the iPP matrix the EbP fractions are segregated from the iPP matrix cumulating mainly on the interfaces between previously formed EPR domains and crystalline iPP matrix. This process results in the multi-layered core–shell morphology of ICP copolymers. It is known that EbP fractions can behave as compatibilizers, which can enhance the interfacial adhesion between the EPR and iPP phases. Thus, the outer shell of the multi-layered core-shell structure can be considered as a compatibilizing layer binding the EPR phase (intermediate layer) with the iPP matrix [27, 17, 18, 29, 24, 30, 33]. The similar phase morphology formed in the bulk ICP copolymer indicates that this multiphase separation of different components of ICP occurs also in the polymer melt. This process together with the morphology of the multiphase also determines the mechanical properties of ICP material [27].

Fan et al. [29] observed that the interaction between the EPR and iPP phases is important for the effective absorption of energy by the tough EPR phase mainly at low temperatures. The significantly better impact-resistant properties of in-situ ICP blends in comparison with mechanically prepared blends can be explained by the presence of the segmented copolymer, which is produced only during the two-stage synthesis of ICP.

Feng et al. [35] studied the influence of EbP addition on the mechanical properties of ICP material. They observed that a suitable amount of EbP diblock copolymer added into the iPP/EPR blend increases toughness and decreases the glass transition temperature. Another advantage of the addition of EbP diblock copolymer into iPP/EPR blend is the increase in tensile strength.

Investigation of PP/EbP/EPR ternary blends revealed that these blends consist of two main phases (iPP and EPR) and the EbP in these blends behaves as a compatibilizer and also as a nucleation agent as well as an emulsifying agent. All these effects of EbP increase the toughness and tensile strengths of the PP/EbP/EPR blend. This effect was directly proved by a detailed SEM analysis of specimens after the tensile test [35].

2 OUTLINE OF THESIS

This thesis will focus on the preparation and characterization of a new type of polymer material based on polypropylene-block-poly(propylene-co-ethylene) (PP-block-EPR). The unique PP-block-EPR copolymers were prepared by using the "stopped-flow" technique. For this purpose a new experimental apparatus suitable for carrying out very short polymerization experiments with a maximum yield will be built.

The synthesized polymer will be characterized in details to confirm the predicted presence of block copolymers. Subsequently, this material will be used for the targeted modification of commercial impact-resistant polypropylene copolymers (ICP) and the effect of block copolymer addition on the properties of the resulting mixture will be studied.

3 EXPERIMENTAL PART

3.1 CHEMICALS AND MATERIALS

All polymerization experiments were performed in liquid propylene using a commercial high-activity $MgCl_2$/phthalate/$TiCl_4$ catalyst (content of titanium in dry catalyst 1.6 wt. %).

Polymerization grade propylene obtained from the PP plant (Unipetrol RPA a.s., Litvínov, Czech Republic. Polymerization grade ethylene was purchased from SIAD Czech spol. s r.o. (Czech Republic). The isopentane used as medium for dissolving ethylene was obtained from the PE plant (Unipetrol RPA a.s., Litvínov, Czech Republic). The triethylaluminum (TEA) co-catalyst with ultra-low aluminium hydride content (<0.05 wt. %, TEA-ULH grade) originated from Chemtura GmbH (Germany).

The surface active agent N,N-bis(2-hydroxyethyl)-$C_{13\text{-}15}$ alkyl amine was purchased from Croda International as Atmer 163. Nitrogen was supplied by Linde Gas a.s. (Czech Republic). It was further purified passing through purification columns with Cu catalyst and a 3A molecular sieve. The content of O_2 and H_2O in the nitrogen were under 0.1 ppm vol.

The reference sequential impact resistant copolymer (ICP) powder was produced at the PP plant of Unipetrol RPA a.s., Litvínov, Czech Republic. The basic properties of this material are summarized in Table 1.

Table 1: Properties of commercial ICP material.

	MFR 21N [g/10min]	X.S. [wt%]	C2 (FT-IR) [wt%]	RCC2 (FT-IR) [wt%]	RC (FT-IR) [wt%]	intrinsic viscosity (X.S.) [ml/g]
ICP	30.6	12.6	7.0	55.8	12.5	229

3.2 STRUCTURAL ANALYSIS METHODS

3.2.1 GPC/SEC – Molecular Mass Distribution Determination

GPC/SEC analysis was carried out at PL-GPC 220 with detectors PL-220DRI and VISKOTEK model 220R, 3x column PL gel 10 µm MIXED-B, 300 x 7.5 mm, mobile phase TCB, flux 1.0 ml/min.

3.2.2 ^{13}C-NMR – Propylene/Ethylene Structure Determination

The propylene/ethylene copolymer structure in ICP and the composition of E/P copolymers synthesized in a stopped-flow apparatus was determined by ^{13}CNMR spectroscopy (Bruker DRX NMR 500 MHz) at 125 °C. PP samples were dissolved in 1.7 mL of 1,2,4-trichlorobenzene and 0.4 mL of deuteron benzene and homogenized for 8 h at 130 °C under nitrogen.

3.2.3 FTIR - Fourier Transform Infrared Spectroscopy

The presence and content of comonomer in the polymer was determined using a Nicolet Nexus FT-IR spectrometer. Transmittance spectra were measured at a resolution of 2 cm^{-1} with 32 scans.

3.2.4 DSC - Differential Scanning Calorimetry

DSC analysis was carried out according to ISO 11357. The DSC measurement of 1st melting, crystallization and 2nd melting was done on a DSC Q 100 TA Instruments calorimeter (TA Instruments, USA). A 5 – 10 mg sample was heated within the temperature range -70 – 200 °C at a rate of 10 °C/min.

3.2.5 TREF - Temperature Rising Elution Fractionation

Analytical TREF was used to characterize the block copolymer prepared by the stopped-flow technique. The 0.04 wt. % polymer sample solution in 1,2,4-trichlorobenzene was prepared and 2.0 mL of this solution were injected into the SS column 300×10 (ID) mm containing an inert support (Chromosorb P 60/80). The initial temperature was 140 °C and the sample was cooled to 40 °C at a rate of 6 °C/h. Afterwards the sample was heated from 40 °C to 140 °C at a rate of 4 °C/min applying 1 mL/min solvent flow through the column.

Preparative TREF was used for fractionation of block polymer samples into three fractions. The preparative column SS 300x20(I.D.) mm was filled with an inert support (Chromosorb P 60/80). The 1 – 2 wt. % solution of the sample in 1,2,4-trichlorobenzene was cooled at a rate of 2 °C/h from 140 °C down to 20 °C. The fractions obtained at 40, 100 and 140 °C were subsequently precipitated by cold methanol, filtered through a sintered glass frit and dried.

3.2.6 Rheological Measurement

Sample used for rheological measurement was in the form of hot-pressed circlet with 21 mm diameter and ca. 2 mm thick.

Viscoelastic properties were measured on a Gemini ETC Bohlin rotational rheometer with the plate-plate geometry (plate diameter 25 mm). Frequency sweep test was performed at 230 °C with constant strain 10 % and an angular frequency in the range between 0.01 – 100 rad/s. Dependence of loss (G’’) and storage (G’) modulus, complex viscosity (η^*), phase angle on frequency were determined.

The point of intersection of loss (G’’) and storage (G’) moduli profiles could be utilized for the calculation of polydispersity index.

3.2.7 DMA - Dynamic Mechanical Analysis

Dynamic-mechanical analysis was carried out on samples prepared via hot pressing according to ISO 293. Measurements were performed on a DMA DX04T instrument (RMI, Czech Republic). A temperature range -88 °C to +120 °C with a rate of heating of 2 °C/min and a single cantilever mode were used.

3.2.8 SEM - Scanning Electron Microscope

The test specimen was cooled to the temperature of liquid nitrogen. After 30 min of cooling the test specimens were broken using a Charpy pendulum. The fracture surface was cut with a sharp broken piece of glass under liquid nitrogen. Then amorphous EPR rubber was etched with xylene (80 °C, 45 min). The etched surface was observed with a Philips XL 30 scanning electron microscope.

The distribution of EPR domains in ICP material was evaluated on three independent SEM pictures.

The sizes of the individual EPR domains were obtained by analysing the image of the SEM microscope through the ATLAS programme (Tescan, Czech Republic). The cavities were marked in the programme. The software evaluates the area, the equivalent diameter (diameter of a circle equal to the same area), the circuit and the position of the frame of the individual cavities. The output is a text file that contains all the values in pixels. The text file has been loaded into the programme AnalyzaCastice, created by Dr Žídek (Faculty of Chemistry, Brno University of Technology, Czech Republic). This software was required to convert the scale (pixels to micrometres). In the next step, the file is copied to an Excel file, which is evaluated by the frequency of the individual particle size.

The final EPR domain distribution profile is the average of these three SEM pictures.

3.2.9 Mechanical Properties

Test specimens were prepared from hot-pressed plates according to ISO 1873.

The flexural modulus was measured on specimens with dimensions of 50x10x4 mm according to ISO 178 on an Instron 3366 instrument (Instron, USA)

Tensile test was carried out at 23°C according to ISO 527 on an Instron 3366 instrument (Instron, USA).

Fracture toughness was evaluated according to the ISO 180 standard at -20 °C

3.2.10 Blending of commercial ICP with PP-block-EPR copolymer

A Brabender Plasti-Corder double-rotor kneader with oil heated kneading chamber (50 cm^3) was used for the preparation of model ICP blends with the PP-block-EPR copolymers produced in stopped-flow polymerizations. The mixture of ICP with PP-block-EPR copolymer was kneaded for 5 min at 220 °C. Before the kneading, blends were stabilized by 0.3 wt. % of Irganox B225 antioxidant.

3.3 POLYMERIZATION APPARATUS

Within the scope of this thesis a high-pressure stopped-flow polymerization apparatus for the homopolymerization of propylene and synthesis of polypropylene-block-poly(propylene-co-ethylene) was constructed.

All the stopped-flow polymerizations performed within this thesis were carried out in liquid propylene. The schema of constructed stopped-flow apparatus is shown in Figure 14.

The modified stopped-flow polymerization apparatus for synthesis of block copolymer contained 100-litre (100L) deactivation high-pressure vessel with a quenching agent (isopropanole), 6-litre (6L) tempered, mixed vessel, which was used for the suspension of dry catalyst in the liquid propylene, 8-litre (8L) tempered and mixed vessel for ethylene, which was dissolved in isopentane and dosing system of triethyl-aluminium (TEA).

The stopped-flow polymerization occurred in the glass capillary reactor with a 3.5 mm inner diameter (see Figure 3). The tube was placed in the 100 L high-pressure vessel. Pressure in the vessel was determining the pressure of polymerization process because polymerization tube was opened into this 100L vessel. The polymerization reaction was initiated by reaction of suspension of catalyst in propylene and TEA in the special mixing zone (right part of Figure 3).

The homopolymerization time can be adjusted by changing the length of the capillary reactor. The time of polymerization, which is shorter than average lifetime of the growing polymer chains (ca. 0.1 s), is very important for polypropylene-block-poly(propylene-co-ethylene block copolymers formation. After then comonomer was added to homopolymer flow in the next mixing block. The copolymerization time can be adjusted by changing the length of the capillary reactor again. The polymerization tube was lead to under surface of quenching agent in the 100 L vessel, for quick terminated of polymerization.

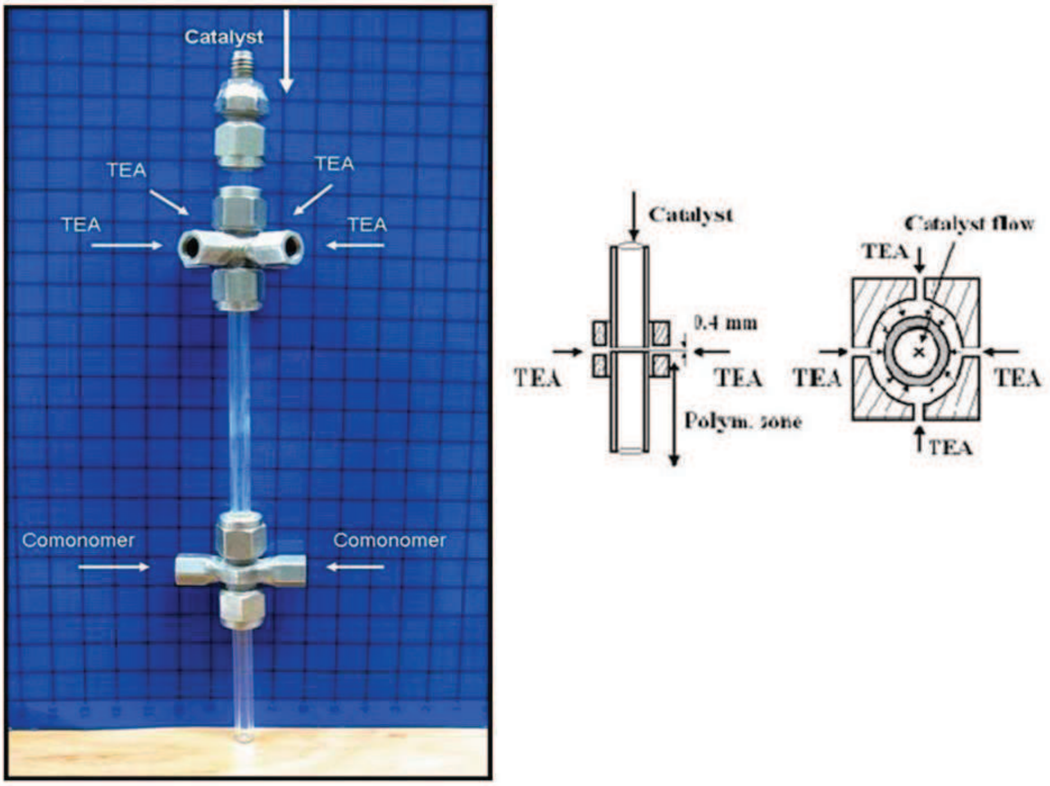

Figure 3: Picture of glass capillary polymerization reactor (on the left) and design of co-catalyst injection system (on the right).

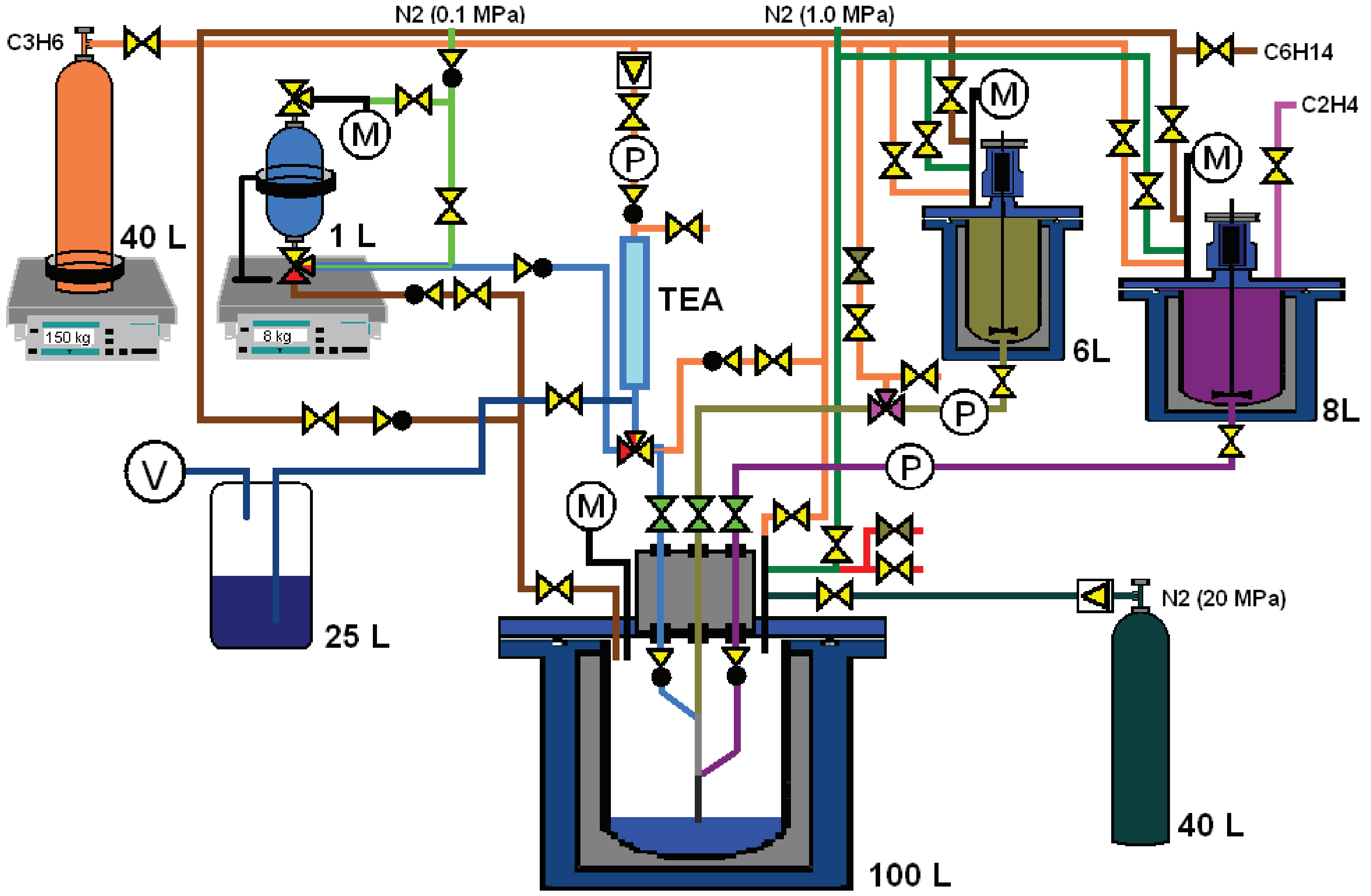

Figure 4: Schematic illustration of the high pressure stopped-flow polymerization apparatus for homopolymerization and block copolymerization.

4 RESULTS AND DISCUSSION

4.1 STOPPED-FLOW HOMOPOLYMERIZATION

After completion of the stopped-flow apparatus and optimization of the stopped-flow polymerization procedure, the initial basic study focused on the evaluation of the relationship between polymerization time and polymer yield was performed. The results shown in Figure 5 indicate, that a lot of experiments trace the relatively long period within which the polymerization rate is increasing. In reality, it almost looks like the polymerization reaction started after ca. 0.10 s after the catalyst and TEA co-catalyst flows mixing. As Mori et al. [3] determined that the formation of active sites (i.e. reaction of the catalyst with the co-catalyst) occurs within a very short period (ca. 0.01 s), it is obvious that some physical phenomena caused a retardation of the activation reaction of the catalyst with the co-catalyst and the formation of active sites in our stopped flow experiments. We assume that the diffusion limitation in liquid propylene around catalyst particles is the main reason that slows the catalyst activation in the stopped-flow capillary reactor.

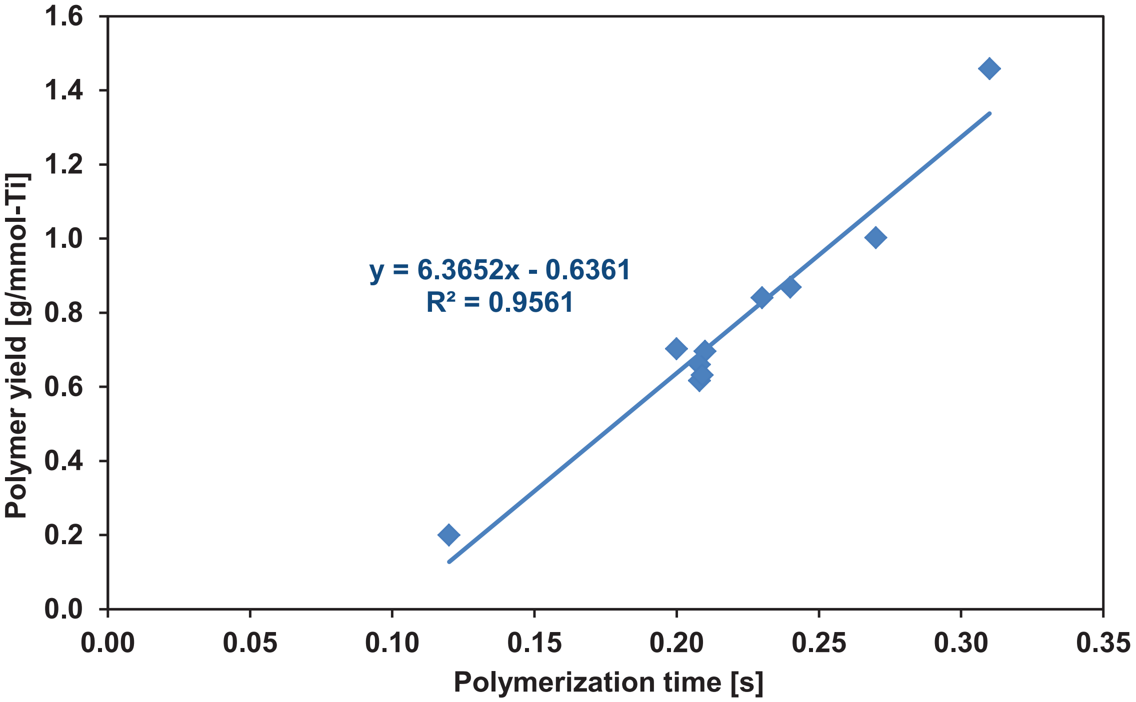

Figure 5: Dependence of homopolymer yield on polymerization time in the capillary reactor of the stopped-flow apparatus. Experimental conditions: Capillary diameter 3.5 mm, polymerization temperature 30 °C, pressure 1.6 MPa (g), catalyst flow 0.3 mmol-Ti/h, Al/Ti molar ratio 450 mol/mol.

4.2 STOPPED-FLOW BLOCK COPOLYMERIZATION

The main focus of this work was targeted at block copolymer synthesis because the obtained products were subsequently further utilized for blending with commercial ICP.

The block copolymerization was performed mainly with an ethylene comonomer. Besides this, several runs with 1-butene were also performed for comparison. Figure 6 shows the influence of the applied comonomer on polymer yield produced in stopped-flow capillary reactors with different polymerization times set by the lengths of the capillaries.

It was found that the copolymerization of propylene with ethylene and 1-butene apparently differs in activity. Experiments with ethylene and 1-butene were performed under similar conditions, and thus it is possible to directly compare polymerization activity and comonomer incorporation. Figure 6 indicates that catalyst activity in the copolymerization of ethylene is ca. 4.3 times higher than in the copolymerization of 1-butene. It is a well-known fact that the 1-butene molecule is apparently less reactive than the ethylene molecule; therefore 1-butene incorporation into the polymer chain is noticeably slower (see Table 2).

Table 2: Influence of a comonomer type on catalyst activity and its incorporation in the polymer chain. Experimental conditions: polymerization temperature 35 °C, pressure 1.6 MPa (g), catalyst flow 0.3 mmol-Ti/h, Al/Ti 760 mol/mol, without Atmer 163.

	Homo time [s]	Copo time [s]	Total time [s]	Comonomer flow [g/h]	Activity [kg/(mmol-Ti*h)]	Comonomer content in polymer [wt%]
Homopolymerization PP	0.20	-	0.20	-	12.6	-
Copolymerization PP-BPR	0.20	0.15	0.35	200	16.4	1.5
Copolymerization PP-EPR	0.20	0.15	0.35	200	22.6	28.0

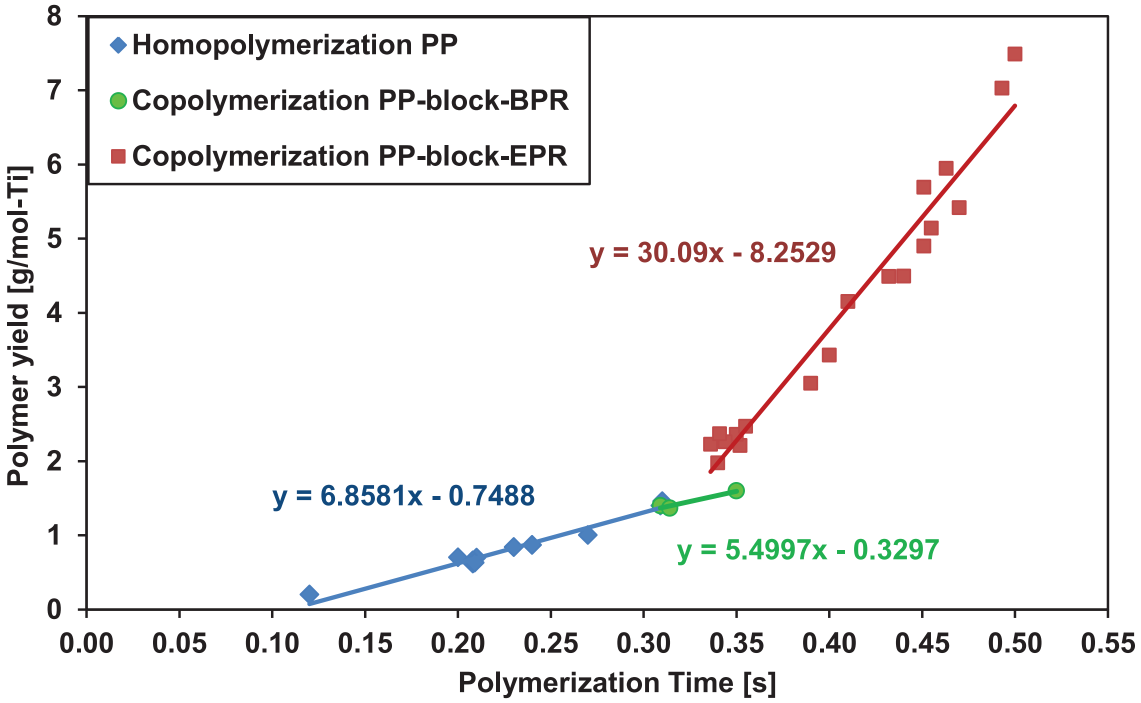

Figure 6: Dependence of polymer yield produced in homo- and copolymerization in the stopped-flow capillary reactor on polymerization time. BPR – butene-propylene rubber, EPR – ethylene-propylene rubber.

4.2.1 Characterization of Block Copolymer via TREF Fractionation

Three samples of block copolymers prepared with different ratios between the blocks of isotactic polypropylene homopolymer and ethylene-propylene rubber were selected for the next detailed analysis. After TREF analysis (Figure 7), the samples were divided into three fractions (F40, F100 and F140 °C) using the preparative TREF method. This method allows the separation of the polymer on the basis of its ability to crystallize at different temperatures as described in Chapter 3.2.5. The ratios of individual fractions obtained by preparative TREF are shown in Table 3.

TREF analysis revealed that the sample K79SF had the highest proportion of amorphous polymer (defined by fraction F40), while on the other hand the sample K104SF had a significant portion of the crystalline fraction F140 (see Table 3). Finally, the K70SF sample had comparable contents of amorphous and crystalline components.

Table 3: Results of the preparative TREF records of three block copolymers produced in the stopped-flow apparatus under different conditions. Polymerization conditions: temperature 35 °C, pressure 1.8 MPa, catalyst flow 0.5 mmol-Ti/h, Al/Ti molar ratio: 1200 mol/mol, [Atmer 163] = 0.03 mmol/L

	Homopolym. time [s]	Copolym. time [s]	Ethylene flow [g/h]	Ethylene concentration [mg/L]	TREF fraction F40 (20-40 °C) [wt. %]	TREF fraction F100 (41-100 °C) [wt. %]	TREF fraction F140 (101-140 °C) [wt. %]
K79SF	0.40	0.15	66	18	41.8	24.6	33.7
K70SF	0.32	0.10	77	21	36.0	26.1	37.9
K104SF	0.38	0.11	44	12	14.4	18.7	66.9

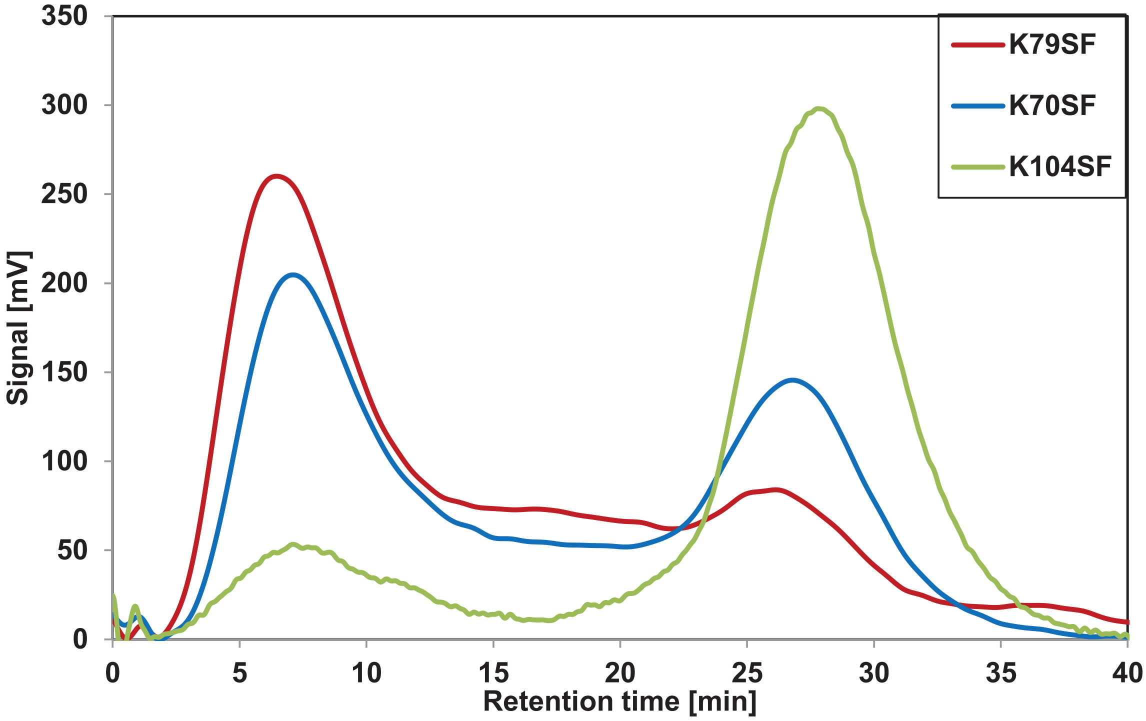

Figure 7: Analytical TREF of block copolymers produced in the stopped-flow apparatus under different polymerization conditions.

Table 4 summarizes the composition and properties of the original materials prepared by stopped-flow polymerization and their fractions obtained by preparative TREF fractionation. The composition of the samples was analysed by ^{13}C-NMR and melting temperature and crystallinity was determined by DSC. Molecular weight and molecular weight distribution was evaluated by GPC.

In the case of samples K79SF and K104SF the amount of incorporated ethylene decreases with increasing the elution temperature. Sample K70SF exhibits the maximum incorporated ethylene in fraction F100. This sample contains the highest amount of ethylene in all fractions. The highest amount of ethylene in the crystalline fractions F100 and F140 indicate that the polymerization conditions applied in the stopped-flow apparatus during the synthesis of the K70SF sample were suitable for producing a significant amount of the real PP-*block*-EPR copolymers.

As shown in Table 4, the fraction F40 consisted mainly of an amorphous random EPR copolymer of a low crystallinity (ca. 4 wt. %). The fraction F100 consisted of a mixture of polymer chains, which have a partial ability to crystallize. The last fraction F140 presumably contained mainly polypropylene homopolymer chains, chains with longer polyethylene sequences and chains of block copolymers PP-*block*-EPR with a long block of PP homopolymer. ^{13}C-NMR analysis revealed that this fraction contained from 2.5 to 15.6 mol. % of ethylene. As it is obvious from Table 4, the amount of ethylene in this fraction directly depends on polymerization conditions. The analyses indicated that polymer materials produced in the stopped-flow apparatus contain significantly more ethylene in the F140 fraction than commercial sequential (ICP) copolymers, where only ca. 0.4 mol. % was determined (see Table 5). This indicates that the samples prepared in the stopped-flow apparatus probably contain a significant quantity of PP-block-EPR copolymers.

The polydispersity index (Mw/Mn) of the TREF fractions was determined by GPC analysis. The polymer fraction F40, which contains mainly amorphous EPR polymer, has a broad molecular weight distribution (Mw/Mn = 7.3). The high polydispersity observed in the case of the F40 fraction could be explained on the basis of a simple assumption: The EPR is produced during the copolymerization period, which follows homopolymerization, and thus the probability of chain transfer reactions increases with the prolonging of the time of polymerization. It is probable that the transfer reactions occur mainly during copolymerization (due to the longer total polymerization time and the possibility of transferring with the comonomer), which results in a broader MWD of the amorphous F40 fraction. Conversely, as was mentioned above, during the homopolymerization period transfer reactions virtually do not occur, hence, the crystalline fraction F140 has a significantly lower polydispersity index (Mw/Mn = 3.0).

The crystallinity of the F140 fraction directly depends on ethylene comonomer flow. As was also mentioned above, 13C-NMR analysis revealed that the fraction F140 comprises mainly of isotactic PP chains, chains with longer polyethylene sequences and chains of block copolymers with a long block of PP homopolymer. At higher concentrations of ethylene comonomer the incorporation of ethylene into the EPR block increases, which results in a decrease in the crystallinity of the whole block copolymer.

Table 4: Characterization of original copolymer samples and their TREF fractions by ^{13}C-NMR, DSC and GPC methods.

		Amount of fraction	^{13}C-NMR		DSC - 2nd melting			GPC			
			Ethylene	Propylene	ΔHm	Tm	Crystallinity	M_n	M_w	M_z	M_w/M_n
		[wt. %]	[mol. %]	[mol. %]	[J/g]	[°C]	[%]	[kg/mol]	[kg/mol]	[kg/mol]	
K79SF	original	100.0	21.0	79.0	13.2	162.1	6.4	36	325	1123	9.0
	F40	41.8	35.2	64.8	8.7	67.1	4.2	22	157	512	7.3
	F100	24.6	21.5	78.5	59.9	121.2	29.0	60	267	624	4.5
	F140	33.7	2.9	97.1	83.9	164.1	40.5	110	331	688	3.0
K70SF	original	100.0	33.4	66.6	33.0	162.7	15.9	48	228	924	4.7
	F40	36.0	43.0	57.0	10.0	60.4	4.8	-	-	-	-
	F100	26.1	51.2	48.8	25.2	151.4	12.1	-	-	-	-
	F140	37.9	15.6	84.5	72.3	164.8	34.9	-	-	-	-
K104SF	original	100.0	9.0	91.0	82.6	160.2	39.9	68	590	1921	8.7
	F40	14.4	23.8	76.2	-	-	-	-	-	-	-
	F100	18.7	20.3	79.7	47.1	124.2	22.7	21	222	876	10.7
	F140	66.9	2.4	97.6	97.2	160.3	47.0	95	305	640	3.2

Table 5: Characterization of commercial ICP sample and their TREF fractions by ^{13}C-NMR.

		Amount of fraction	^{13}C-NMR	
			Ethylene	Propylene
		[wt. %]	[mol. %]	[mol. %]
ICP	original	100	25.8	74.2
	F40	25.9	59.2	40.8
	F100	10.6	48.8	51.2
	F140	63.5	99.6	0.4

4.3 BLENDS OF COMMERCIAL ICP WITH PP-*BLOCK*-EPR COPOLYMER

Three mixed samples with comparable portions of PP-*block*-EPR copolymers were synthesized in the stopped-flow apparatus and subsequently used for the preparation of model mixtures with ICP. For the testing it was necessary to produce ca. 5 g of each PP-*block*-EPR copolymer sample by mixing of 3-5 separated runs in the stopped-flow apparatus, then 3 g were used for kneading with ICP and the rest of the sample was used for the TREF fractionation and characterization. Table 6 shows the conditions applied during stopped-flow experiments and the subsequent amount of amorphous F40 (20 – 40 °C) and the crystalline fraction F100 + F140 (41 – 140 °C), determined by preparative TREF. The fractions containing chains that could crystallize (fraction 41 – 140 °C) were analysed by ^{13}C-NMR in order to determine the composition and content of total incorporated ethylene (see Table 7).

As shown in Figure 8, the samples K9x and K10x were prepared with a short copolymerization time resulting in production of a minimal amount of amorphous EPR (fraction F40). The low content of free EPR chains (i.e. without covalently bonded PP homopolymer) was important in order to be able to evaluate the effect of PP-*block*-EPR copolymers on the properties of ICP. For comparison, the K8x sample with a higher content of amorphous EPR was also selected for blending with ICP.

Table 7 summarizes the composition and properties of original materials prepared by stopped-flow polymerization and their crystalline fractions (fraction 41 – 140 °C) obtained by preparative TREF fractionation. The composition of the samples was determined by ^{13}C-NMR. Furthermore, melting temperature, melting enthalpy and crystallinity was determined by DSC.

As shown in Table 7, the K8x sample contains the most of ethylene in the crystalline fraction obtained by preparative TREF. It is possible that this sample contains the highest amount of the block copolymer PP-*block*-EPR. Samples K9x and K10x contain a significantly lower amount of ethylene in the crystalline phase, and probably a smaller amount of block copolymer.

Although the crystallinity of the crystalline part of samples K8x and K9x is almost the same, sample K9x contains less than half of the ethylene in the crystalline portion compared to K8x. This fact indicates that the composition of the EPR block (primarily the ratio between the ethylene and propylene in EPR) is dependent on the conditions of the synthesis of the polymer in the stop-flow apparatus. However, it is evident that the ratio between incorporated ethylene and propylene in the EPR block does not have to effect the crystallinity of the crystalline fraction of the block copolymer. The K10x sample probably contains shorter EPR blocks and longer blocks of isotactic polypropylene, which increases its crystallinity. This sample also has the lowest amount of incorporated ethylene in the crystalline fraction.

Table 6: Polymerization conditions in stopped-flow experiments and contents of F40 (amorphous) and F100+140 (crystalline) fractions determined by preparative TREF. Experimental conditions: temperature 35 °C, pressure 1.8 MPa (g), catalyst flow 0.5 mmol-Ti/h, Al/Ti molar ratio: 1200 mol/mol, [Atmer 163] 0.03 mmol/L.

				TREF fraction	
	Homopolym. time [s]	**Copolym. time [s]**	**Ethylene flow [g/h]**	**F40 (20-40 °C) [wt. %]**	**F100 + F140 (41-140 °C) [wt. %]**
K8xSF	0.30	0.15	44	26.2	73.8
K9xSF	0.35	0.10	44	15.6	84.4
K10xSF	0.40	0.10	44	14.4	85.6

Table 7: Characterization of the original samples and theirs crystalline TREF fractions (F100+140, range of elution temperature 41 – 140 °C) by ^{13}C-NMR and DSC.

			^{13}C-NMR		**DSC - 2nd melting**		
		Amount of fraction [wt. %]	**Ethylene [mol. %]**	**Propylene [mol. %]**	**ΔHm [J/g]**	**Tm [°C]**	**Crystallinity [%]**
K8xSF	original sample	100.0	22.7	77.3	53.8	158.9	26.0
	F100 + F140	73.8	19.6	80.4	71.0	160.7	34.3
K9xSF	original sample	100.0	17.0	83.0	64.5	159.6	31.1
	F100 + F140	84.4	9.6	90.4	70.3	159.8	34.0
K10xSF	original sample	100.0	9.0	91.0	82.6	160.2	39.9
	F100 + F140	85.6	6.1	93.9	97.2	160.3	47.0

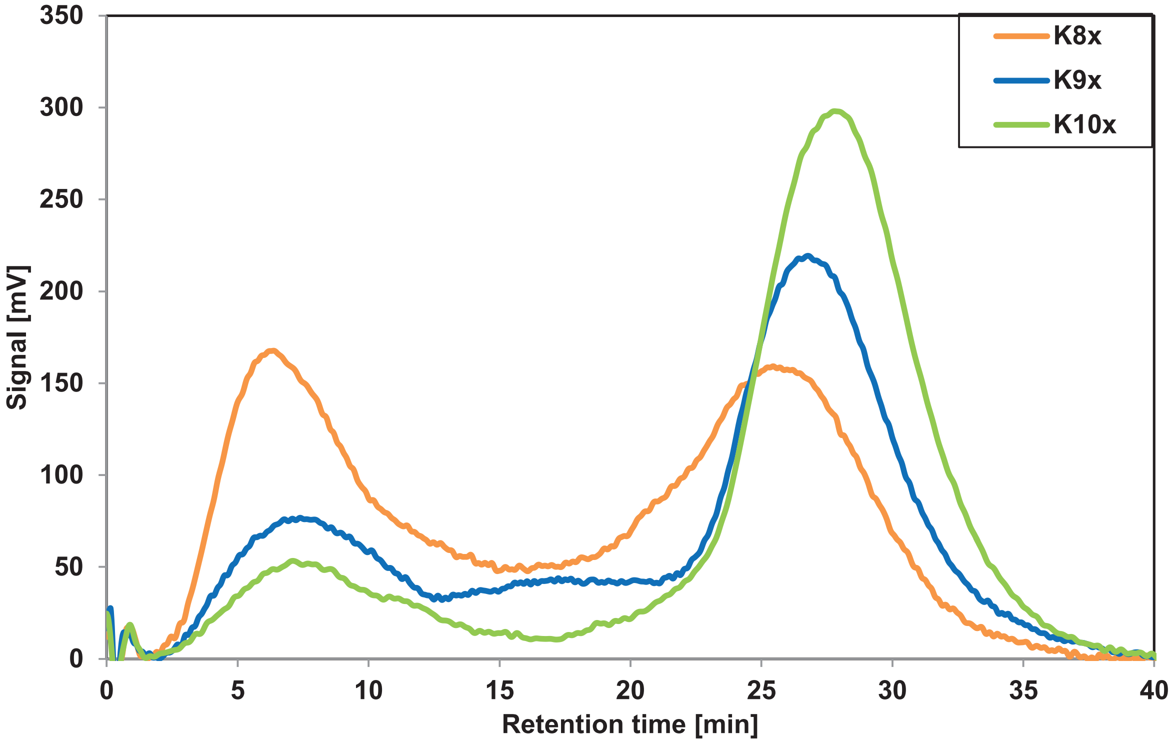

Figure 8: Fractionation of prepared samples by analytical TREF.

4.3.1 EPR Domain Size Distribution via SEM

In this chapter, the influence of block copolymer composition on the dispersion and size of EPR domains in a commercial ICP was studied by SEM. After the SEM picture processing and calculation of EPR domain sizes the EPR domain size distribution profiles were computed and can be seen in Figure 9. It is obvious that the original ICP sample (i.e. without addition of any block copolymer) contains a significant portion of EPR domains smaller than 0.5 µm. Conversely in the case of ICP samples blended with PP-*block*-EPR copolymers mainly EPR domains with sizes bigger than 0.5 µm were observed in the samples. The average domain sizes (d50), shown in Table 8, indicate that EPR domains d50 of all the ICP samples with added block copolymers have d50 ca. four times higher in comparison with original ICP. Such an obvious difference in EPR domains size distributions is an interesting observation, because Jang et al. [28] consider 0.5 µm to be the critical diameter for EPR domains in ICP. He assumes that only EPR domains with a diameter bigger than 0.5 µm could improve the fracture resistance of heterogeneous ICP materials.

Moreover, Chen et al. [34] published that the mechanically dispersed EPR phase in the PP matrix typically does not form domains bigger than 0.2 µm. Fan et al. [29] proposed that the main reason for the small EPR domains formed in mechanically prepared PP/EPR blends is the absence of the EbP component.

The results obtained within this study agree with the theory of Fan et al. [29]. It is evident that the amount of block copolymers in standard ICP materials is rather low, and thus small EPR domains are formed preferentially. Then the addition of an extra portion of block copolymer into the ICP sample caused significantly bigger EPR domains to be formed.

Table 8: Average size of EPR domains (d50) evaluated from SEM pictures. The amount of ethylene in PP-block-EPR copolymer was determined by ^{13}C-NMR analysis in the crystalline fraction (41-140 °C) of samples prepared in the stopped-flow apparatus.

	E in EPR-block in ICP	**Average EPR domain size (d50)**
	[wt. %]	**[µm]**
ICP	0.00	0.23 ± 0.05
K10x (1 %)	0.04	0.77 ± 0.05
K10x (2 %)	0.07	0.88 ± 0.05
K9x (2 %)	0.11	0.85 ± 0.03
K8x (2 %)	0.21	0.86 ± 0.02

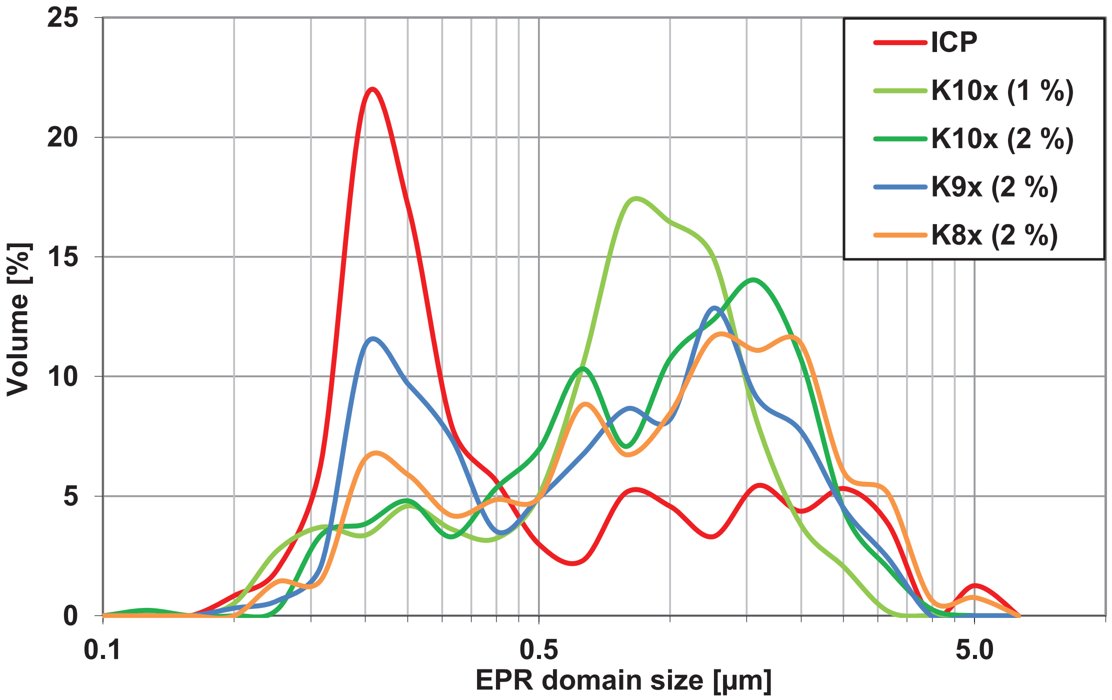

Figure 9: Profiles of EPR domain distributions for the original ICP and ICP with added PP-block-EPR copolymers.

4.3.2 Oscillation Rheology and Dynamic Mechanical Analysis

The results of oscillation rheology (see Figure 10**)** and Dynamic-mechanical analysis (see Figure 11**)** show relatively small differences among all the studied samples. The higher modulus observed in the case of ICP samples containing added PP-block-EPR copolymers could be related to "increasing" molar mass upon block copolymer addition and the subsequently increasing amount of "tangled" macromolecules upon real block addition or to presence of further iPP, which was added together with the PP-block-EPR copolymer and which caused some nucleation effect due to its very high molar mass.

However, no difference was observed between the samples with the addition of the block copolymers K8x and K10x with different contents of iPP as shown in Table 12 (65 wt. % vs. 84 wt. %). Thus, it can be assumed that the presence of the block copolymer PP-block-EPR increases the modulus of the mixture also at temperatures below T_g of iPP.

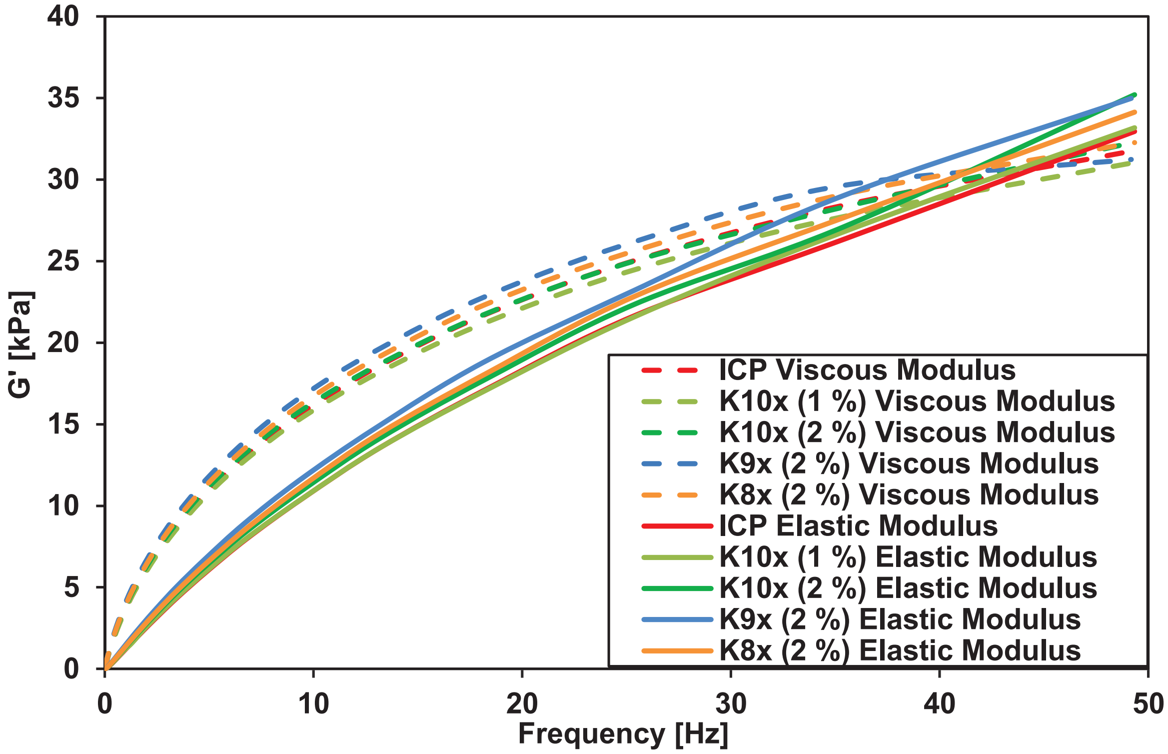

Figure 10: Dependence of the elastic (G') and viscous (G") modulus on frequency.

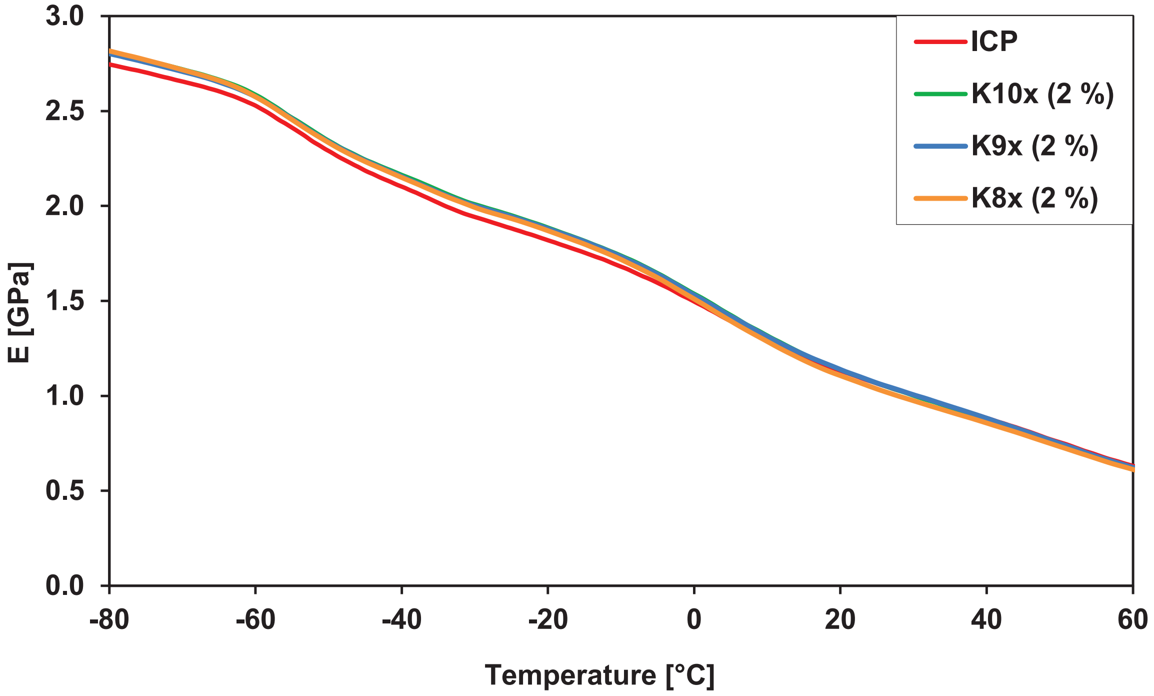

Figure 11: Dependence of complex elasticity modulus (E) on temperature for the original ICP sample and the ICP samples with added PP-block-EPR copolymers.

4.3.3 Mechanical Properties

The reference ICP material and the ICP blends which contained defined amounts of PP-*block*-EPR copolymers prepared in stopped-flow polymerizations were used for the preparation of test specimens for determination of mechanical properties. Test specimens were cut from hot pressed plate and tested according to the ISO 178 standard.

The dependence of the flexural modulus on the amount of ethylene added to the ICP as a part of the PP-block-EPR copolymer is shown in Table 9 and Figure 12. As is obvious from Figure 12, the ICP samples with added PP-block-EPR copolymer exhibited a flexural modulus noticeably lower in comparison with the original ICP. It was found that addition of a small amount of the PP-*block*-EPR copolymer caused an obvious decrease in flexural modulus by ca. 120 MPa. A further increase of the PP-*block*-EPR copolymer in ICP did not cause any further decrease in the flexural modulus.

The Charpy notched impact strength was measured at -20 °C and the results are shown in Table 9. Figure 13 indicates its steep increase with the increasing content of the PP-*block*-EPR copolymer. Addition of a small amount of PP-*block*-EPR copolymer increased the Charpy notched impact strength by 0.5 kJ/m^2 to 2.7 kJ/m^2. A further addition of the block copolymer caused only a small increase to 2.9 kJ/m^2. The increase of the notched impact strength is in accordance with the decrease in the flexural modulus. The higher toughness of the ICP material with added PP-*block*-EPR copolymer was also confirmed by the elongation at break dependence shown in Table 9. The elongation at break decreases by 43 % by adding a small amount of the PP-*block*-EPR copolymer. As in previous cases a further addition of block copolymer caused only a small change in the elongation at break value.

Table 9: Dependence of mechanical properties and average EPR domain size on the amount of ethylene in the crystalline fraction (41-140 °C) of samples prepared in the stopped-flow apparatus and the total amount of EPR in ICP. The total amount of EPR in ICP was calculated from the triad distribution (^{13}C-NMR analysis) using 1st order Markovian statistics

	E in EPR-block in ICP [wt. %]	EPR total in ICP [wt. %]	Flexural modulus [MPa]	Izod impact strength notched (-20°C) [kJ/m^2]	Elongation at break [%]	Tensile Stress at Yield [MPa]	Average EPR domain size [μm]
ICP	0.00	12.50	1546 ± 32	2.1 ± 0.1	13.6 ± 3.1	25.0 ± 0.4	0.23 ± 0.05
K10x (1 %)	0.04	12.61	1428 ± 37	2.7 ± 0.2	7.8 ± 2.7	24.3 ± 0.1	0.77 ± 0.05
K10x (2 %)	0.07	12.72	1418 ± 42	2.9 ± 0.2	8.2 ± 2.3	24.1 ± 0.2	0.88 ± 0.05
K9x (2 %)	0.11	12.96	1469 ± 36	2.8 ± 0.1	7.8 ± 1.5	24.0 ± 0.2	0.85 ± 0.03
K8x (2 %)	0.21	13.04	1474 ± 50	2.9 ± 0.2	6.5 ± 2.4	24.7 ± 0.4	0.86 ± 0.02

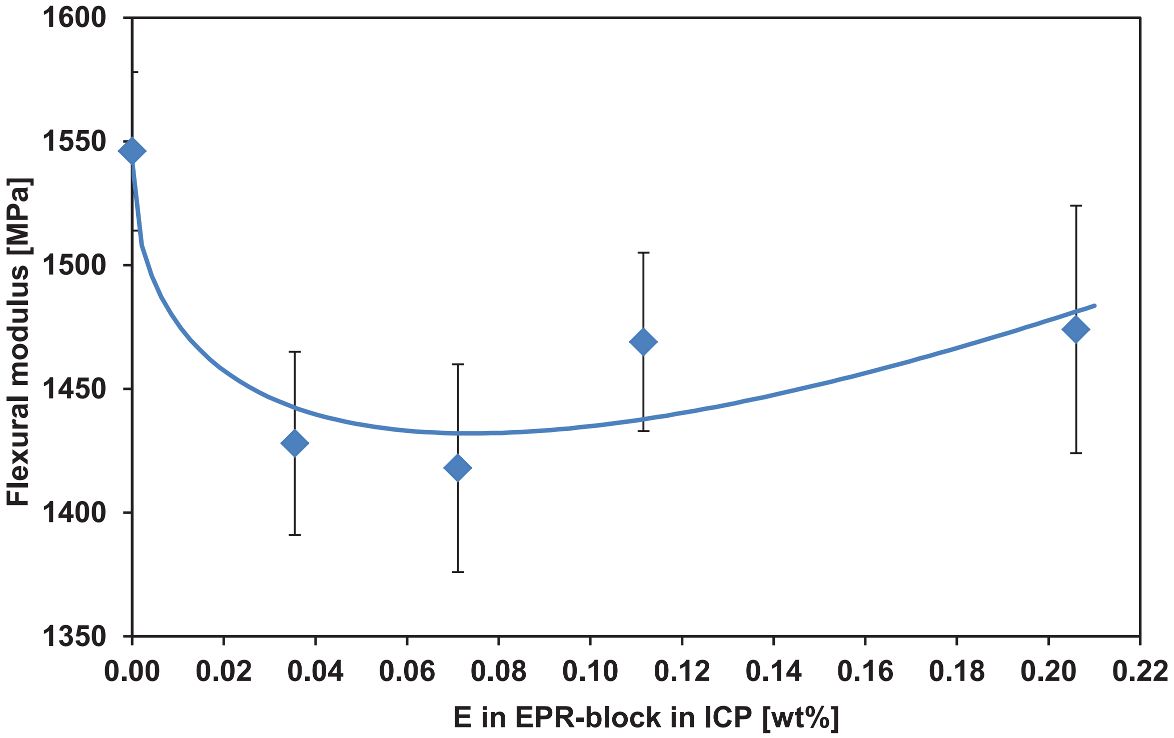

Figure 12: Dependence of flexural modulus on the amount of ethylene in the PP-block-EPR copolymer added to the ICP.

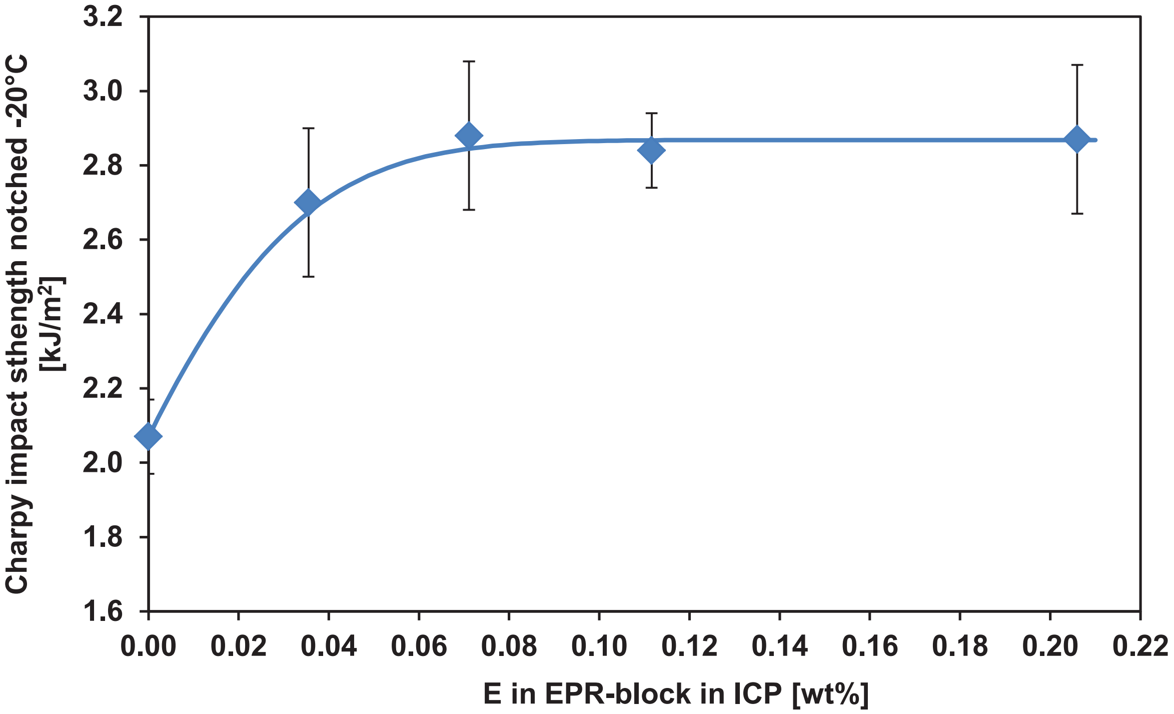

Figure 13: Dependence of the Charpy impact strength notched (measured at -20°C) on the amount of ethylene in the PP-block-EPR copolymer added to the ICP.

5 CONCLUSION

The main objective of this work was to construct a unique high pressure stopped-flow apparatus enabling polymerization in very short polymerization times on a commercial $MgCl_2$/phthalate/$TiCl_4$ catalyst. The stopped-flow technique enables the performing of polymerization in a shorter time than the average lifetime of the growing polymer chain, which ensures that the states of active sites are not significantly influenced by time-dependent changes and chain-transfer reactions.

The first part of the experimental study was focused on the homopolymerization of propylene. It was found that polymerization time was in the range of 0.10 - 0.35 s and the polymerization exhibits "quasi-living" character.

This is important for the synthesis of well-defined PP-*block*-EPR copolymers. The apparatus also enabled the production of sufficient amounts of materials for characterizing and subsequent blending with ICP. The very short polymerization times applied in stopped-flow capillary reactors ensured that the active sites of a Ziegler-Natta catalyst produced polymer chains consisting of a block of semi-crystalline polypropylene homopolymer and a block of amorphous random copolymer. The block copolymerization was performed mainly with an ethylene comonomer, but polymerizations with 1-butene were also performed for comparison.

It was found that the copolymerization of propylene with ethylene and 1-butene apparently differs in activity. Catalyst activity in the copolymerization of ethylene is more than four times higher than in the copolymerization of 1-butene. It is a well-known fact that the 1-butene molecule is apparently less reactive than the ethylene molecule, and therefore 1-butene incorporation into the polymer chain is noticeably slower.

Copolymer materials synthesized in the stopped-flow apparatus with ethylene comonomer were fractionated by preparative TREF. The fractions obtained were subsequently analysed by the DSC, ^{13}C-NMR and GPC methods. These analyses revealed the presence of incorporated ethylene, also in the crystalline fraction (100 – 140 °C), presumably bonded to homopolymer crystalline chains which brought the macromolecules to the crystallizable fractions. This finding confirmed that a significant portion of polymer chains produced in the stopped-flow polymerization were real block copolymers consisting of semi-crystalline PP homopolymer and amorphous-to-partially crystalline EPR copolymer in one polymer chain.

The three samples with a known quantity and quality of composition were blended in a melt with a commercial ICP material.

The differences in EPR domain morphology and placement in the PP matrix were studied by SEM as shown **Chapter 4.3.1**. The obvious influence of the PP-*block*-EPR copolymer on ICP properties was observed mainly in the morphological changes of the EPR domains dispersed in the PP matrix. It was found that the original ICP sample contains a significant portion of EPR domains smaller than 0.5 µm. Conversely, in the case of ICP samples blended with PP-block-EPR copolymers, mainly EPR domains with sizes bigger than 0.5 µm were observed in the samples. The average domain size d50 of the EPR domains of all the ICP samples with added block copolymers have a d50 ca. four times higher in comparison with the original ICP.

The results of oscillation rheology and Dynamic-mechanical analysis (**Chapter 4.3.2)** show relatively small differences among all the studied samples. The higher modulus observed in the case of ICP samples containing added PP-block-EPR copolymers could be related to "increasing" molar mass upon block copolymer addition and the subsequently increasing amount of "tangled" macromolecules upon real block addition or to presence of further iPP, which was added together with the PP-block-EPR copolymer and which caused some nucleation effect due to its very high molar mass.

However, no difference was observed between the samples with the addition of the block copolymers K8x and K10x with different contents of iPP as shown in Table 12 (65 wt. % vs. 84 wt. %). Thus, it can be assumed that the presence of the block copolymer PP-block-EPR increases the modulus of the mixture also at temperatures below Tg of iPP.

The reference ICP material and the ICP blends, which contained defined amounts of PP-*block*-EPR copolymers prepared in stopped-flow polymerization, were used for the preparation of test specimens for the determination of mechanical properties (**Chapter 4.3.3**). The ICP samples with added PP-block-EPR copolymer exhibited a flexural modulus noticeably lower in comparison with the original ICP. It was found that addition of a small amount of the PP-block-EPR copolymer caused an obvious decrease in flexural modulus by ca. 120 MPa. A further increase in the PP-block-EPR copolymer in ICP did not cause any further decrease in flexural modulus.

The Charpy notched impact strength was measured at -20 °C and the results indicate its steep increase with the increasing content of the PP-block-EPR copolymer. Addition of a small amount of the PP-block-EPR copolymer increased the Charpy notched impact strength more than five times. The increase of the notched impact strength is in accordance with the decrease of the flexural modulus. The greater toughness of the ICP material with added PP-block-EPR copolymer was also confirmed by the elongation at break dependence. The elongation at break decreases by 43 % by adding a small amount of PP-block-EPR copolymer. Based on the model, it was found that changes in mechanical properties were not caused simply by the addition of the amorphous phase of EPR to the sample of commercial ICP.

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7 LIST OF SYMBOLS AND ABBREVIATIONS

7.1 ABBREVIATIONS:

BCC	– body-centred cubic conformation	
BCP	– block copolymer	
BPR	– butene-propylene rubber	
C2	– ethylene	
C3	– propylene	
Cat.	– catalyst	
DBP	– di-*i*-butyl phthalate	
DTMA	– Dynamic Mechanical Analysis	
DSC	– Differential Scanning Calorimetry	
E	– ethylene	
EB	– ethylene-1-butene copolymer	
EbP	– ethylene-propylene block copolymer	
ED	– external donor	
EH	– ethylene-1-hexene copolymer	
EPR	– ethylene-propylene random copolymer	
EsP	– ethylene-propylene segmented copolymer	
F_a	– xylene insoluble fraction	
F_b	– xylene soluble fraction	
FT-IR	– Fourier transform infrared spectroscopy	
g	– gas phase	
GPC/SEC	– gel permeation chromatography / size exclusion chromatography	
ICP	– impact copolymer polypropylene	
iPP	– isotactic polypropylene	
MFR	– melting flow rate	[g/10min]
MWD	– molecular weight distribution	
NMR	– nuclear magnetic resonance	
P	– Propylene	
PE	– polyethylene	
PP-b-EPR	– polypropylene – block-poly(propylene-co-ethylene)	
PTFE	– Polytetrafluoroethylene	
RC	– content of EPR in ICP	
RCC2	– content of ethylene in EPR copolymer	[wt. %]
SF	– stopped-flow	
SEM	– Scanning electron microscope	
SSA	– Successive Self-nucleation Annealing	
TEA	– triethylaluminium	
TREF	– temperature rising elution fractionation	
X.S.	– xylene soluble	
ZN	– Ziegler-Natta	
μ-CT	– Computer micro-tomography	

7.2 SYMBOLS:

G'	– elastic modulus	[Pa]
G''	– viscous modulus	[Pa]
H	– enthalpy	
H_u, H_i	– heats of fusion for repeating monomer unit[J.cm^{-3}]	
k	– Boltzmann constant	[J/K]
M_n	– number-average molar mass	[g/mol]
M_w	– weight-average molar mass	[g/mol]
M_w/M_n	– polydispersity index	
p	– pressure	[Pa]
PI	– polydispersity index	
R	– gas constant	[J/K*mol]
t	– time	[s]
T	– temperature	[°C]
T_g	– glass-transition temperature	[°C]
$T_{m,I}$	– melting temperature	[°C]
V_m	– molar volume	[m^3/mol]

7.3 GREEK LETTERS:

η	– viscosity	[Pa.s]
η^*	– complex viscosity	[Pa.S]
λ	– number-average dispersed phase of growing chains	
ρ	– density	[g/cm^3]
ρ_c	– density of crystals	[g/cm^3]
σ_e	– basal surface energy of polymer crystals	[mJ/m^2]
τ	– average lifetime of growing polymer chain	[s]

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9 CURRICULUM VITAE

Personal Details

Name: Ing. Adam Hoza
Date of birth: 3.6.1984
Address: Bučovická 1247, 684 01 Slavkov u Brna, Czech Republic
Telephone: +420 608 232 543
E-mail: adam.hoza@polymer.cz

Education

From 2010 study in the Doctoral Degree Programme, Faculty of Chemistry, Brno University of Technology

- In the field Macromolecular Chemistry

2008-2010 full-time study in the Master's Degree Programme, Faculty of Chemistry, Brno University of Technology

- In the field Chemistry, Technology and Properties of Materials
- Final state examination

2004-2008 full-time study in the Bachelor's Degree Programme, Faculty of Chemistry, Brno University of Technology

- In the field Chemistry, Technology and Properties of Materials
- Final state examination

2000-2004 Secondary Technical School of Chemistry, Brno

- School-leaving exam

Working experience

2007-2009 POLYMER INSTITUTE BRNO, spol. s r.o. – Service and advance working in the plastic manufacturing. (Temporary)

2010-2015 POLYMER INSTITUTE BRNO, spol. s r.o – Researcher (Temporary)

From 2015 UNIPETROL RPA, s.r.o. – POLYMER INSTITUTE BRNO, odštěpný závod – Researcher