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Structures Copolymers used as Binders in Polyurethane Coatings

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Abstract

This work describes the preparation and properties of structured copolymers. The theoretical part describes the structures and possibilities of synthesis, a basic description of molecular weights and their determination, a description of the properties of polyurethane coatings. The use of structured copolymers as a binder in paints is described in the experimental part. Furthermore, the experimental part contains the characteristics of the prepared structured copolymers in terms of molecular weight distribution, the characteristics of the prepared coatings using basic painting tests, determination of the glass transition temperature (T_g) of the prepared coatings, determination of micro hardness.

Keywords

Structure copolymers, SEC-MALS, Film-forming properties, ionic polymerization, GTP polymerization

Klíčová slova

Strukturované kopolymery, SEC-MALS, filmotvorné vlastnosti, iontová polymerace, GTP polymerace

Table of Contents

Introduction

The range of application properties of synthetic polymers is influenced not only by their molar mass distribution, but also by the structure of the polymer chain. The structure affects the properties of the polymer chain, such as: branching, chemical resistance, solubility, thermodynamic behaviour in solution, melt viscosity, creep.

The first synthesized structured polymer was a star-shaped polymer, synthesized in 1948. It was synthesized by Schaefen and Flory. [1] Since then, there has been a large increase in publications dealing with the synthesis of star polymers and other structures using various techniques. Known polymerization techniques include, for example: Group Transfer Polymerization (GTP) or Reversible Addition Fragmentation Chain Transfer (RAFT). RAFT polymerization is currently also used for the synthesis of polymers used in photovoltaics and medicine.

Due to the fact that these polymerization techniques are relatively expensive, and there is the possibility of synthesizing structured polymers also by ionic polymerization, which is significantly cheaper compared to previous polymerization techniques, this technique is often used.

1. Polymer structures

There are many polymeric structures that can be synthesized using various polymerization techniques. The basic and most well-known polymeric structures include the following types: block co/polymer, branched polymer, dendrimers, helical co/polymer, hyperbranched polymers, star polymers, polymer networks, linear polymers, grafted and comb polymers. There are also so-called exotic structures, which may include the following polymers: cardo polymers, cetane polymers, ladder polymers, multi-strand polymer, roxatanes, spiro polymers and centipede polymers. [2 - 5]

The star polymers are formed by a core to which the arms are attached. [6] The core may be a nano gel, a small molecule or a polyol, as in the case shown in Figure 1, where the number of OH groups determines how many arm stars are formed. In this way it is possible to prepare three, four, five, six…. arm stars. If a more functional acrylate is used as the core, for example: ethylene glycol dimethacrylate (EGDMA), a star-shaped polymer with a high number of arms is formed. [7] The number of arms can only be influenced by the amount of more functional acrylate added. When adding a more functional acrylate, the possibility of side reactions must also be taken into account. The side reactions that occur with the addition of a large amount of difunctional acrylate include the so-called core-core coupling. This means that in the reaction mixture there is too much so-called core forming agent and these reaction centers begin to react with each other, resulting in the formation of a polymer network and a gel. [6-11] The structures of star-shaped polymers are shown in Figure 1.
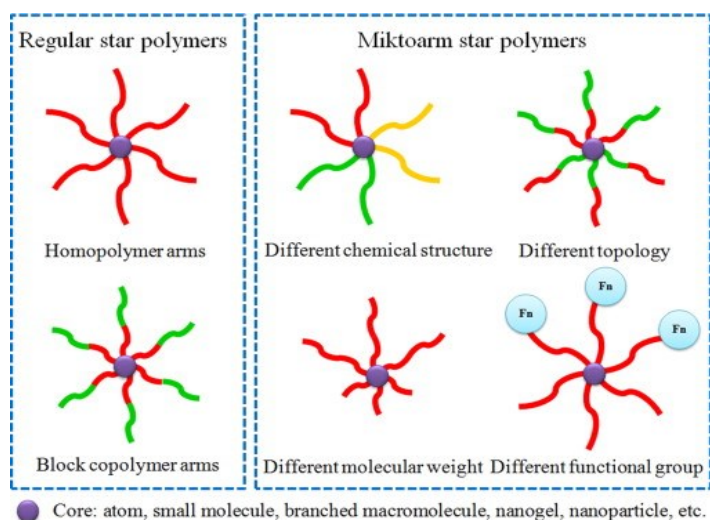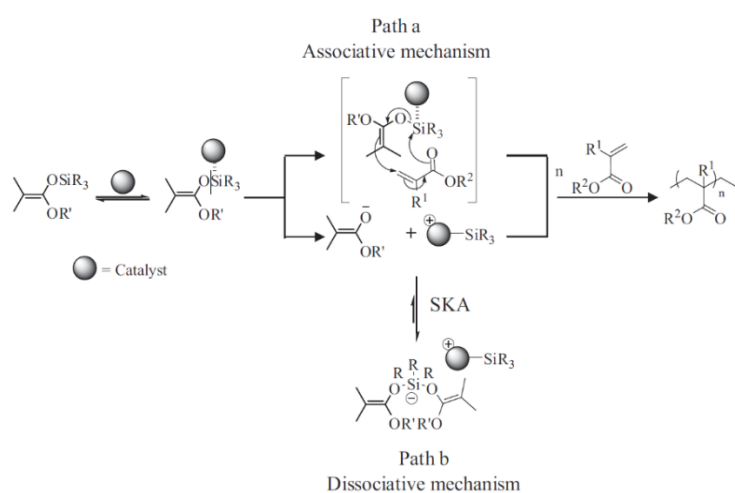
Figure 1 Structures of star polymers. [12]

1.1 Synthesis techniques of polymerizations structures

In the commercial process, radical polymerization is one of the most widely used polymerizations. The main factors in the use of radical polymerization are their wide applicability to monomers and various reaction conditions. Radical polymerization is simple and inexpensive compared to other technologies. By conventional radical polymerization, however, it is not possible to synthesize polymeric structures. Therefore, it is appropriate to use other polymerization techniques such as e.g. Group Transfer Polymerization (GTP), Reversible addition-fragmentation chain-transfer polymerization (RAFT), Atom transfer radical polymerization (ATRP), Single Electron Transfer-Living Radical Polymerization (SEC-LRP), Oxoammonium catalysed oxidation (called organic synthesis, in macromolecular chemistry known as Nitroxide-Mediated Radical Polymerization (TEMPO and 4-OH-TEMPO)), ionic polymerizations (cationic and anionic). [3]

1.1.1 Group Transfer Polymerization - GTP

GTP polymerization is still used for the synthesis of various structures, despite its relatively high cost. Recent discoveries include the 1992 discovery that a polymer that initiated polymerization was used for a GTP catalyst. The discovery belongs to T. Kakuchi and Yasud from Hokkaido University, Japan. Research into *N*-heterocyclic carbenes (NHCs) as catalysts has been addressed by a group around D. Taton (University of Bordeaux, France) and a group around R. M. Waymouth (Stanford University, California). These groups used *N*-heterocyclic carbenes (NHCs) catalysts for the polymerization of acrylates, methacrylate's and acrylamides as block copolymers. [13 - 16]

Group Transfer Polymerization can be classified as "quasi-living" oxoanionic polymerizations in terms of mechanism. The technique is suitable for the polymerization of α, β-unsaturated carbonyl substances, where ketene acetals are used together with metal-free nucleophilic catalysts to initiate the polymerization. [17-19] The first theory hypothesized that it is a covalent non-ionic mechanism that is dependent on the protection of the polymer chain by a trimethylsilyl group (present in the initiator) that initiates polymerization. Later experiments showed that it is an oxo-ammonium mechanism (dissociative GTP mechanism), where the enolate acts as an active center of reaction. [20-21] As GTP polymerization experiments continued, N-heterocyclic carbene-catalysed GTP polymerization (NHCs) also emerged over its catalysts over time, suggesting that it is an associative GTP mechanism. [22] The current 2002 theory is that the possible mechanism of GTP polymerization is dissociative and associative at the same time, with the balance shifting more to the dissociative mechanism between the dissociative and associative mechanisms, [23 - 24] as shown in Figure 2.

Figure 2 Possible dissociative and associative mechanism of GTP polymerization. [22]

According to the mentioned features of GTP polymerization, it can be described as a universal method of synthesis of structured copolymers. Structures that can be synthesized by GTP polymerization include, for example: block copolymers, star polymers, linear polymers, functionalized polymers (containing functional groups at the beginning/end of the chain, depending on the initiator used), which can then be used in the next step. as precursors for radical polymerization or ring-opening (usually epoxy ring) polymerization. [3; 25 - 26] The limitation of GTP polymerization is its high sensitivity to the purity of used monomers and solvents, therefore the molecular weight of GTP polymers is usually up to 20,000 g/mol and the dispersity of polymers prepared in this way is usually in the range Đ ~ 1.2 - 1. 3 [26]

GTP polymerization is sensitive to impurities, water and protons. [3; 18] Therefore, monomers and solvents must be thoroughly cleaned, dehydrated and dehydrated before use. Monomers which contain R-OH, R-CO$_2$H groups in their structure must be protected in order to be polymerizable. The most commonly used protecting groups are

trimethylsilyl (TMS), but also, for example: 2-(pyridin-2-yl) ethyl, tetrahydro-2H-pyran-2-yl, which protect carboxyl groups. [7; 27]

Typical GTP solvents used are tetrahydrofuran (THF), 1-2-dimethoxyethane, acetonitrile (MeCN), toluene (PhMe), N, N-dimethylformamide (DMF) and propylene carbonate. It is also possible to use dichloromethane and 1,2-dichloroethane.

Various types of molecules are used as initiators of GTP polymerization. They can be divided into simple mono-functional initiators, mono-functional initiators with a protected group, simple di-functional initiators, and degradable di-functional initiators (they form a ketene acetal in the reaction mixture). GTP initiators usually contain the following structure:

1-alkoxy-1- (trimethylsiloxy) -2-methyl-1-alkene. The simplest GTP initiator is

1-methoxy-1-trimethylsiloxy-2-methyl-1-propene (MTS), from which other GTP initiators can be derived. This gives rise to trimethylsilyl ketene acetals, which are the most widely used, but their disadvantage is that they decompose over time. In bifunctional initiators, a polymer chain grows at both ends of the initiator. Examples of bifunctional initiators are:

1,4-bis (methoxytrimethylsiloxymethylene) cyclohexane (MTSMC) a

1,2-bis [1- (2-methyl-1- (trimethylsiloxy) prop-1-enyloxy) ethoxyethane] (BisMTS). [28 - 29]

Silyl ketene acetals and α-silyl esters and their derivatives such as trimethylsilyl cyanide generate silyl ketene acetals in the reaction mixture. These types of initiators are suitable for the polymerization of acrylates. [28 - 29]

The choice of catalyst for GTP polymerization is important because the catalyst activates the initiator by nucleophilic catalysis and the monomer by electrophilic catalysis. In nucleophilic catalysis, a small amount of catalyst is used, usually ~ 0.1% per initiator, but in electrophilic catalysis, the amount required is significantly higher, usually ~ 10% per initiator. The following can be used as GTP catalysts: soluble fluorides, difluorides, azides, cyanides, phosphines, oxoanions and dioxo anions.

GTP polymerization is usually used for the synthesis of polymers with a molecular weight of 1,000 - 20,000 g/mol, but it can also be used for the synthesis of polymers with a molecular weight of 100,000 - 200,000 g/mol. In the case of polymerizations of high molecular weight monomers, the demands on the purity of the monomers and solvents used increase. It can simply be said that the larger the molecule we want to synthesize, the cleaner the chemicals we need. [30]

Random polymers can be synthesized very easily, it is sufficient to mix the starting monomers and start the polymerization.

The procedure for block copolymers is similar. First, block A is polymerized, followed by a short pause for all A-monomer to react, in the second step monomer B is added and again for monomer B to react, thus forming block copolymer AB with a living end to which a third block C can be synthesized in formation of ABC copolymer, or

terminate the reaction. The literature indicates that up to 9 block copolymers can be synthesized in this way. [17 - 18; 30 - 31]

1.1.2 Ionic polymerization

The term live polymerization, and live polymerization, was first discovered and defined by Schwarz as a polymerization chain that grows without side reactions (transfer and termination). His discovery was that the initiator could be consumed at the beginning of the polymerization, and the polymerization proceeded very quickly even with monomers of different reactivity. The names controlled or live polymerization are currently used. [33 - 36]

Currently, live / controlled polymerizations are considered to be those that meet the following:

- have linear kinetics ln ([M]0/[M] vs time) - Figure 3. If the reaction proceeds in the first step to monomers, it usually shows a slow initiation, which is related to the termination or deactivation of the catalyst
- shows a linear increase in molecular weight with a conversion of Δ[M]/[I]0, with the ratio of molecular weight to conversion indicating transfer, constant chain growth and slow initiation as shown in Figure 4.
- polydispersity may decrease with conversion in slow initiation systems, and increase with conversion when side chain reactions predominate
- end-group functionality is not affected by slow initiation and transfers, but functionality decreases when side reactions begin to predominate [36–38; 39]
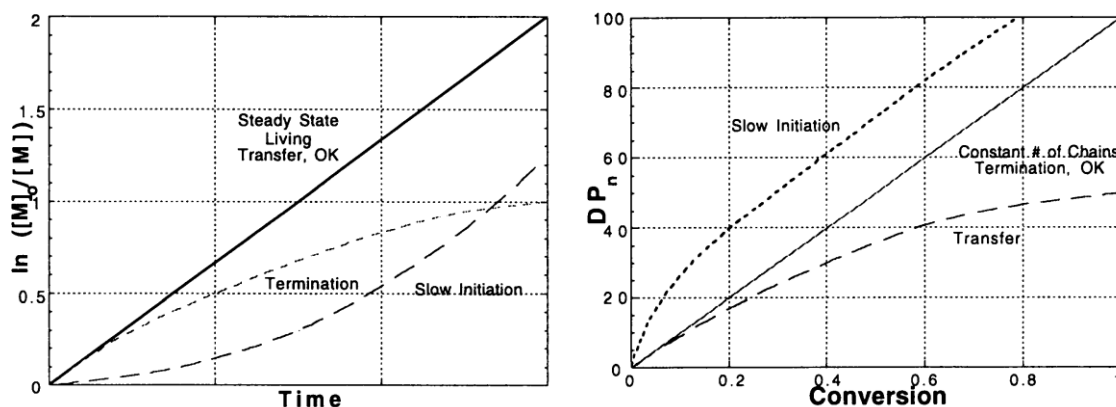
Figure 3 and 4 The kinetics of ionic polymerization, where figure 3 shown kinetics of ionic polymerization, and figure 4 shown dependency initiation on the conversion. [39]

The first truly controlled living polymerization was described in 1982 by Otsu, who polymerized dithiocarbamates by cationic polymerization, achieving high dispersity and low conversion. [40] In 1993, Georges published the first article on the block TEMPO polymerization of styrene. [41] In 1995, the way to use Cu, Ru, CuX_2 / bips, $RuCl_2$ / $(PPh_3)_2$ was started. [42] Later, this type of polymerization was called Atom Transfer

Radical Polymerization (ATRP). This was followed by other polymerization concepts such as: addition / fragmentation (RAFT), degenerative transfer (TEMPO, ATRP).

[43 - 47]

Ionic polymerization uses polarization on the double bond. Initiation of ionic polymerization requires low activation energy and the polymerization rate is little temperature dependent. Ionic polymerization usually takes place at -70 °C / -50 °C. The anionic polymerization usually takes place at -70 °C in THF. Ionic polymerizations do not terminate by recombination because the growing chains are electrostatically repelled from each other due to the charge at their ends.

Termination of growth is caused by impurities and intentionally added substances such as: water, alcohols, amines, oxygen. These substances react with the micro ion at the end of the polymerization chain to form a neutral substance or an inactive ion.

Complexes based on: BF_3, $AlCl_3$, $TiCl_4$, $SnCl_4$, $SbCl_5$, P_2O_5, $AgClO_4$ with alcohol or as oxonium salts have proved successful for cationic polymerization, with positive ions initiating the polymerization. It is also possible to initiate cationic polymerizations with HCl, H_2SO_4 and $KHSO_4$. In cationic polymerization, there is a carb cation or oxonium ion at the end of the chain. [48]

1.1.3 Polyurethanes and polyurethane coatings

Polyurethanes have been studied since 1935. Their use in macromolecular chemistry began to be studied by Otto Bayer and his collaborators in the German group I.G. Farben, where they discovered addition reactions of polyisocyanates with polyalcohol to form high molecular weight products. Polyurethane chemistry is universal in terms of the choice of isocyanates from single-functional, multi-functional to polyisocyanates and alcohols, which can be separated similarly to isocyanates. [49]

Polyurethanes are coatings that contain a urethane group (-NH-COO-). The advantages of polyurethane coatings include good resistance to stress and abrasion resistance. Aromatic isocyanates have one major disadvantage, namely that they change colour to yellow after being exposed to UV radiation. This change is undesirable in some applications, so it is necessary to stabilize them or replace them with aliphatic isocyanates. Hindered Amino Light Stabilizers (HALS stabilizers) are usually used for stabilization, which contain $-NH_2$ groups in their structure, which are able to form stable radicals. [50] Among the disadvantages of aliphatic isocyanates it is possible to include their lower reactivity about up to 2-3 times compared to aromatic isocyanates, but on the other hand their advantage is that they are significantly cheaper than aromatic isocyanates.

Polyurethane coatings are most often used as coatings for furniture, structural coatings for buildings, to a lesser extent as coatings for cars, seals in electrical engineering and others. These uses can be summarized in one-word CASE. CASE is an abbreviation of the English words: coatings, adhesives, sealants and bedding. [51]

In the reaction of a poly / isocyanate to form a polyurethane, an alcohol / poly alcohol (polyol) is most often used. Polyols are most commonly used as oligomers. The number of functional groups affects the properties of the resulting polyurethane, foam, or coating. [63] The polyols used are polyether polyols, aliphatic / aromatic polyester polyols, acrylic polyols, THF-based polyether polyols, polytetramethylene glycol (PTMEG). The largest group of polyols include polyether polyols, which include propylene oxide (PO) and ethylene oxide (EO) derivatives. The most common are heterogeneous mixtures of PO and EO, block copolymers of PO with EO. A combination with butylene oxide (BO) is also possible. Polymeric polyols include copolymers, graft polymers, disperse polyols, polyesters, polymeric polyols, [52-57] polytetramethylene glycol (PTMEG), polytetrahydrofuran (PTHF), [58] natural oils presenting various types of polyols including, for example: castor oil. oil containing natural triglycerides. [59 - 61]

Catalysts are used in the production of PUR foam and in the use of PUR coatings. Usually, dilute catalyst solutions are added in an amount of 0.1-1 % by weight. The most commonly used catalysts are: triethylene diamine, *N*-(2-dimethylaminoethyl) -*N*-methyl piperazine, dimethylamino ethanol, *N*-ethylmorpholine and dibutyltin dilaurate (DBTL). [62]

Urethane coatings include: two-component coatings, isocyanate-blocked coatings, wet-curing PUR coatings, thermoplastic PUR dispersions, PUR/acrylate dispersions, aqueous UV curable PUR coatings and urethane alkyds.

2 Objectives of the work

- Prepare structured copolymers with different arm lengths and number of functional groups
- Characterize the prepared structured copolymers using gel permeation chromatography, gel permeation chromatography in conjunction with multi-angular light scattering and online viscometer, determination of OH group content, determination of acid number
- Synthesize polyalcohols, and characterize them by gel permeation chromatography, determination of acid number and determination of OH group content. The polyalcohols will be added to the star polymers to form PUR coatings
- Synthesize and characterize a star shaped GTP polymer without functional groups, which will be used as a plasticizer in PUR coatings
- Characterize prepared PUR coatings using basic painting tests
- Characterize the prepared coatings by determining the glass transition temperature T_g
- Putting PUR coating (s) into practice

2　Experimental part

2.1 Process for the synthesis of star polymers by ionic polymerization

The following procedure was used for the synthesis of star polymers: The appropriate polyol trimethylol propane (TMP), stannous octoate (SnOct) and substances necessary for the synthesis of the arms were weighed into the sulfonation flask, i.e. 2-H-oxet (OXET), ε-caprolactone (CAPA) in a given ratio. Then, under a gentle supply of inert gas, the polymerization apparatus was heated in a heating mantle to 150 °C and maintained at this temperature for 5 hours. After five hours, the temperature was raised to 180 °C, and was maintained until the acid number dropped below 5 mg KOH/g.

The progress of the polymerization was monitored by SEC, where a decrease in the low molecular weight fraction and an increase in the high molar fraction of the star were visible.

Figure 5 shows a graph of time versus M_n and M_w. The linear course of the graph shows that it is a controlled ionic polymerization.
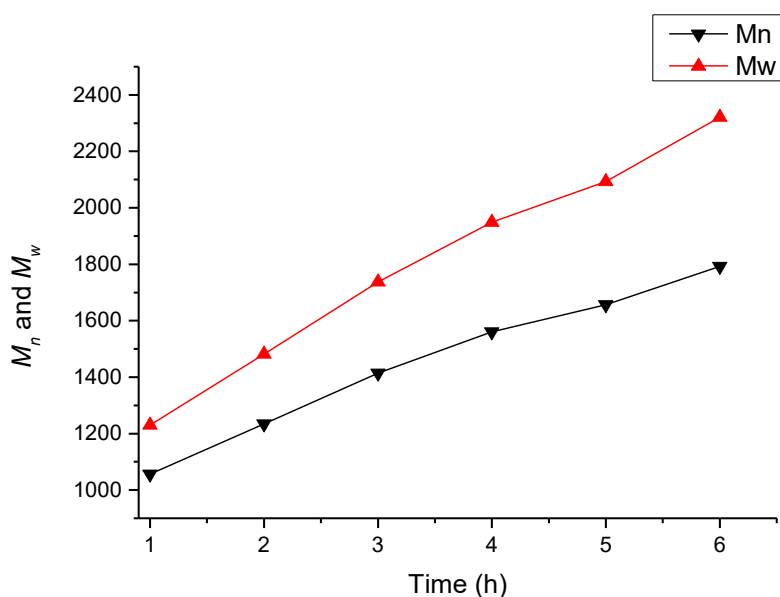
Figure 5 Verification of ionic polymerization kinetics

Subsequently, star polymers characterized by SEC and the SEC-MALS-on-line viscometer method were synthesized. The results of the determination of the molar mass by the SEC method are shown in Table 4, and the results from the determination of the absolute molar masses and intrinsic viscosity are shown in Table 5. The formulations of the prepared star polymers are given in Tables 1-3.

Table 1 Star polymers based on trimethylolpropane (TMP)

Sample name	H-12	H-13	H-14	H-15	H-16
Model	1 + 3	1 + 3 + 6	1 + 3 + 9	1 + 3 +12	1 + 3 +15
Content	TMP Puralact B3 TIB KAT 129	TMP Caprolactone Puralact B3 TIB KAT 129	TMP Caprolactone Puralact B3 TIB KAT 129	TMP Caprolactone Puralact B3 TIB KAT 129	TMP Caprolactone Puralact B3 TIB KAT 129
Look (2nd day)	clear	clear	clear	clear	clear 5th day turbid
Solid state (%)	98.1	98.0	98.9	98.0	98.8
Viscosity (25°C mPa.s)	6,842	6,365	5,675	5,515	6,170
Viscosity (60°C mPa.s)	-	-	-	-	-
Conditions	5h/130°C+0.5h/160°C	5h/130°C+0.5h/160°C	5h/130°C+0.5h/160°C	6h/130°C+0.5h/160°C	6h/130°C+0.5h/160°C

Table 2 Star polymers based on trimethylolpropane (TMP)

Sample name	H-17/1	H-18	H-19	H-20	H-21/B
Model	1 + 3 + 18	1 + 6 + 15	1 + 6 + 18	1 + 6 +24	1 + 3 +36
Content	TMP Caprolactone Puralact B3 TIB KAT 129	TMP Caprolactone Puralact B3 TIB KAT 129	TMP Caprolactone Puralact B3 TIB KAT 129	TMP Caprolactone Puralact B3 TIB KAT 129	TMP Caprolactone Puralact B3 TIB KAT 129
Look (2nd day)	solid, turbit	clear	clear	clear, later turbid	turbid
Solid state (%)	97.5	97.5	98.9	98.7	98.8
Viscosity (25°C mPa.s)	-	21,900	20,285	22,800	-
Viscosity (60°C mPa.s)	1,290	1,480	1,630	2,080	100,800
Conditions	7h/130°C+0.5h/160°C	6h/130°C+0.5h/160°C	6h/130°C+0.5h/160°C	7h/130°C+0.5h/160°C	7h/140°C+0.5h/170°C

Table 3 Star polymers based on trimethylolpropane (TMP)

Sample name	H-3416
Model	1 + 12 + 48
Content	TMP Caprolactone Puralact B3 TIB KAT 129
Look (2nd day)	turbid
Solid state (%)	99.2
Viscosity (25°C mPa.s)	19,422
Viscosity (60°C mPa.s)	3,705
Conditions	7h/130°C+0.5h/170°C

2.1 Characteristics of prepared star polymers

PS standards (Agilent) were used to calibrate the gel permeation chromatography, THF was used as the mobile phase, the columns used were Agilent PLgel Mixed-C 300 x 7.5 mm packed with a styrene-divinylbenzene gel with a particle size of 5 μm. The sample weight for analysis was 3 mg/ml, and the column was injected with 100 μl. Polystyrene calibration was used only to very roughly estimate the molar mass and to monitor changes during synthesis.

In the SEC chromatograms, a decrease of the starting monomers at the end of the chromatogram and a gradual increase of the product were visible, i. stars at the beginning of the chromatogram. The reaction kinetics of ionic polymerization were also performed on the sample. It was found that the resulting dependence of the monitored samples is linear. This means that the reaction is controlled (see Chapter 3.1).

The results of the molecular weight determination by SEC-RI are shown in Table 4. Table 4 shows the basic parameters M_n, Mw, M_z and the dispersity M_w/M_n. The results show a gradual increase in the number - average relative molar mass, the weight - average relative molar mass and the z - average molar mass. The resulting dispersion is in the range of 1.30 - 1.80, which corresponds to higher values of polydispersity in ionic polymerizations. Usually the values of polydispersity range from 1.10 to 1.40. Star polymers with a higher dispersion are polymers with a high CAPA / LAC ratio, the substances forming the arms of the resulting star. Higher dispersity values are probably due to the different CAPA / LAC reaction rate.

Table 4 Experimental data obtained by SEC-RI method for prepared star polymers

Star	M_n	M_w	M_z	M_w/M_n
H 13	1,800	2,300	2,900	1.30
H 14	2,300	3,100	3,900	1.30
H 15	2,700	3,600	4,400	1.30
H 16	3,100	4,200	5,200	1.30
H 17	3,800	5,100	6,300	1.40
H 18	3,800	5,100	6,500	1.40
H 19	3,000	3,300	3,500	1.10
H 20	5,100	7,100	9,100	1.40
H 21	7,200	11,000	15,600	1.50
H 3416	8,000	14,000	19,100	1.80

2.1 Characteristics using SEC-MALS-OnlineViskozimeter

The SEC-MALS-RI-on line viscometer system was used to determine the absolute molar masses, THF was used as the mobile phase and the sample injection into the column was 100 µl.

Table 5 shows the absolute values of molar masses, polydispersity M_w/M_z and intrinsic viscosity $[\eta]$ (ml/g).

The differences in molar masses between the SEC in Table 4 and the SEC-MALS-RI-on line viscometer in Table 5 are due to the SEC system being calibrated to PS standards. In the analysis of the samples, the elution time of the PS standards was compared with the elution time of the sample. The molar masses obtained by the SEC method are correct but indicative. They are indicative of the fact that the samples are star-shaped polymers, but the PS standards are linear, and this fact entails inaccuracies in the determination of molar masses by SEC.

On the other hand, the SEC-MALS-RI-on line viscometer system does not need to be calibrated to PS standards, the system works with light scattering, and this provides us with absolute values of molar mass M_w. This system is suitable for the characterization of structured, branched copolymers.

Table 5 Experimental data obtained by SEC-MALS method for prepared star polymers

Star	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	M_w/M_n	$[\eta]$ (ml/g)
H 13	1,300	1,500	1,700	1.14	5.8
H 14	1,600	1,900	2,200	1.17	6.9
H 15	1,900	2,200	2,500	1.15	7.0
H 16	2,400	2,600	3,000	1.11	8.5
H 17	2,700	3,000	3,300	1.11	9.6
H 18	2,800	3,100	3,600	1.14	10.1
H 19	3,000	3,500	3,600	1.18	9.1
H 20	3,700	4,300	4,900	1.15	11.8
H 21	5,700	6,600	7,700	1.16	17.2
H 3416	6,700	8,800	10,900	1.31	10.2

Figure 6 shows the cumulative molar distributions of trimethylolpropane (TMP) -based star polymers. As the ratio of Arm-forming chemicals changes, the molar mass gradually increases in the series. The increase in molar mass is due to a gradual increase in the amount of arm-forming chemicals in the reaction mixture. This growth of arm-forming chemicals is visible in Tables 1-3, where the formulation of TMP-based star polymers is shown.
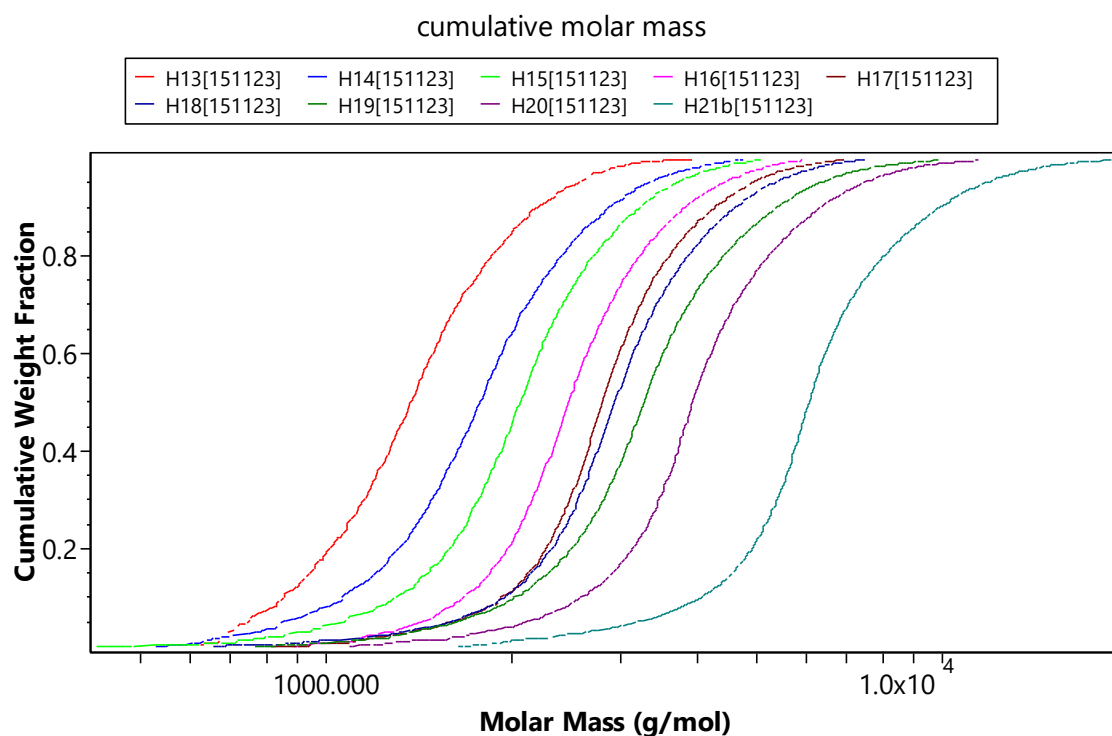
Figure 6 Cumulative molar mass distribution of star polymers based on TMP

## 2.2 Optimization of curing conditions for polyurethane coatings

Two studies were performed to set the curing conditions of PUR coatings. The first focused on the effect of temperature and cure time and the second on the effect of IPDI. 3 types of stars were selected to study the effect of temperature and curing time. One pseudostar, one star based on pentaerythritol and one star based on dipentaerythritol were selected. Three test temperatures of 80 °C, 90 °C and 110 °C and three cure times of 3 hours, 6 hours and 8 hours were selected. Times of 3 and 8 hours were used for 80 °C and 90 °C, a combination of 3 hours and 6 hours for 110 °C.

As shown in Table 6, for stars H-2310, H-14 and H-415, which were cured at 80 °C at 3 and 6 hours, this did not affect the hardness of the prepared coating. The prepared coatings remain sticky and soft even after firing. It was difficult to evaluate them because they adhered to the needle of the micro hardness tester and due to their softness, the hardness of the glass was measured and not the coating. Curing at a higher temperature helped, where the coatings showed minimal tack, but virtually no hardness of the prepared coating film.

Table 6 Results of the dependence of micro hardness on the temperature and curing time of coatings based on a pure star with IPDI on glass

Temperature (°C)	80		90		110	
Time (h)	3	8	3	8	3	6
H-2310	sticky	sticky	0.5	0.8	0.6	0.6
H-14	1.2	0.0	1.7	1.9	1.9	2.2
H-415	0.0	0.0	3.5	3.2	2.6	2.9

For better clarity of the results, Figure 7 was created, which shows the dependence of time and temperature on the hardness of the prepared coating.
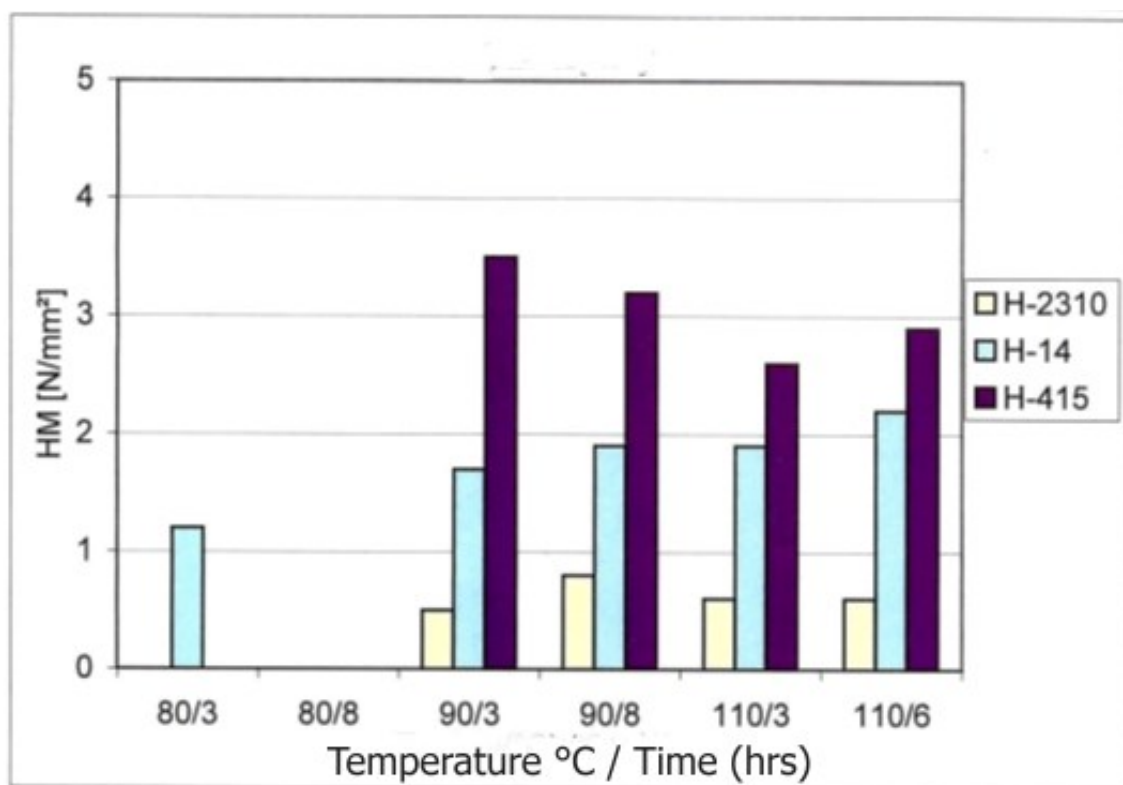
Figure 7 Dependence of temperature and curing time on the hardness of the coating film

It can be seen from Figure 7 that higher temperatures and longer firing times do not have a significant effect on the hardness of the prepared coatings. Therefore, a temperature of 80 °C and a time of 3 hours were chosen under optimal conditions. When firing the coatings, this temperature and time proved to be correct, as all formulated coatings based on three, five and hyperbranched stars were cured under these conditions.

2.2.1 Influence of IPDI on coating hardness

Two-star types H-415 and H-21 were selected to set the amount of IPDI. IPDI with a content of 34.04% NCO was used. The content of NCO groups was determined potentiometrically in Synpo a.s according to the internal directive. Labelling H-415-1 and H-21-1 means a standard addition of IPDI according to the paint formulation, and labelling H-415-2 with H-21-2 means a 10% excess of IPDI in the formulation.

The effect of isocyanate addition on the hardness of prepared coatings is shown in Chart 7.

Chart 7 Dependence of the hardness of the coating on the IPDI content, where number 1 means the standard addition and number 2, a 10% excess of IPDI

Star	OH (mg KOH/g)	HM (N/mm^2)	E (GPa)
H-415-1	71.6	1.1	0.0
H-415-2	71.6	1.3	0.0
H-21-1	105.2	2.0	0.0
H-21-2	105.2	2.0	0.0

A slight excess of IPDI increased the hardness of the coatings, so this option was chosen in the coating film formulation, but also because a 10 % excess of isocyanate is usually used in the formulation of PUR coatings.

2.3 Evaluation of properties of coating films based on trimethylolpropane

TMP was chosen as the basis of the star polymer, which was branched by the addition of CAPA and LAC in different ratios, so that there was a gradual decrease in the hydroxide number in the series. Table 8 shows the summarized results of the TMP-based council. Determination of abrasion using taber abraser was not possible with this series, due to the low hardness of the coatings, for this reason the coatings were torn and glued to the rollers of the taber abraser. The bend on the cylindrical mandrel was greater than 2 mm for all prepared coatings, which indicates that the coatings have a good adhesion to the surface.

Table 8 Properties of pure paint films based on TMP

Star	OH (mgKOH/g)	HM (N/mm^2)	E (GPa)	Bend (mm)
H-13	134.4	2.4	0.2	< 2
H-14	105.2	1.2	0.0	< 2
H-15	84.5	2.0	0.0	< 2
H-16	77.5	1.2	0.0	< 2
H-17/1	64.9	1.3	0.0	< 2
H-18	63.2	1.6	0.0	< 2
H-20	47.5	1.4	0.0	< 2
H-21/B	33.4	1.5	0.0	< 2
H-3416	24.9	1.1	0.0	< 2

Chart 8 shows the decrease in hydroxide number of the prepared TMP-based star polymers. This decrease is due to a change in the ratio of the starting materials forming the star's arms. The resulting micro hardness of the coatings is in the range of 1.1-2.4 N/mm^2, these values are very low, the resulting coatings are soft and showed good adhesion to the surface and anti-slip properties. Table 10 shows that the decrease in hydroxide number does not have a significant effect on the change in microhardness of the prepared coatings.

3   Conclusion

Ion polymers prepared star polymers based on trimethylol propane (TMP), of which there were 10. The prepared star polymers were characterized by the SEC method and the SEC-MALS-RI-on line viscometer. Absolute molar masses, dispersity, intrinsic viscosity and cumulative molar mass distributions were obtained from this method. By changing the amount of arm-forming chemicals, there was a gradual increase in molar mass in a series of star polymers, as seen in Figure 6, which shows the cumulative molar distributions of TMP-based star polymers.

Optimization of the curing conditions of the polyurethane coatings into which the synthesized star polymers were used was performed. Dibutyltin dilaurate was used as a polymerization catalyst as a 1 % solution in methyl ethyl ketone.

In the next step, an experiment was performed to determine the effect of the amount of isophorone diisocyanate (IPDI) on the hardness of the resulting coating. It was found that a higher amount of IPDI slightly increases the hardness of the resulting coatings. For this reason, a 10 % excess of IPDI in the coating formulation was chosen. A 10 % excess was also chosen because this excess is also commonly used in practice in the formulation of polyurethane paints.

Ten polyurethane coatings based on pure star polymers were formulated. The resulting coatings were soft after firing, and therefore it was not possible to determine the abrasion resistance on the Taber Abraser. The microhardness of the prepared coatings ranged from 1.1 to 2.4 N/mm^2. These values are low. In the bending test on the cylindrical mandrel, the resulting bending was <2 mm for all coatings, which indicates the elasticity of the coatings. The determination of the hydroxyl number OH mg KOH/g was necessary to calculate the amount of isocyanate needed to cure the coating.

These coatings showed interesting properties, despite their softness, their surface appeared to be non-slip. Their potential use is possible, for example: in showers.

To verify that the monomers react with controlled ionic polymerization, polymerization kinetics studies have been performed which have shown to be controlled ionic polymerization.

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