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ORIGINAL CONTRIBUTION

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Polyurethane anionomers synthesised with aromatic, aliphatic or cycloaliphatic diisocyanates, polyoxyethylene glycol and 2,2-bis(hydroxymethyl)propionic acid

Part I. Synthesis and macro-molecular structure

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Abstract Taking advantage of the step-growth polyaddition method, which has been developed earlier, and applying it in the reaction of aromatic, cycloaliphatic and aliphatic diisocyanates with polyoxyethylene glycol, 2,2-bis(hydroxymethyl)propionic acid and 1,6-hexamethylene-diamine, a few polyurethane anionomers were synthesised, which were recovered from aqueous dispersions in the form of thin polymeric films. Analytical chemistry methods, like gel permeation chromatography with *N*,*N*-dimethylacetamide as the polar eluent and high-resolution nuclear magnetic resonance and IR spectroscopy, were employed to confirm their chemical structures, to find molecular weights and their distribution and to characterise the polarity of the chemical structure of the polyurethane chain formed.

Keywords Polyurethane anionomers · Chemical structure · GPC analysis · ^{1}H-NMR · IR spectroscopy

Introduction

Polyurethane (PU) anionomers include the group of linear PUs, or those with lower densities of cross-linking, which have very small numbers of acidic functional groups, e.g. COO^{-} or HSO_3^{-}, in their chains [1]. In general, the structure of a PU anionomer chain, alike that of any elastomer, is composed of blocks, and it comprises both rigid urethane segments (derived from diisocyanates and diamines) and flexible polyether or polyester segments:

$$-R_1-NH-CO-O-R-O-OC-NH-R_1-NH-CO-NH-R_3-NH-OC-NH-R_1-NH-CO-COO^{-} \quad (1)$$

where:

R1 Aromatic, alicyclic or aliphatic radical derived from diisocyanate employed in the synthesis

R2 Aliphatic chain derived from polyol, e.g. oligo-oxypropylene glycol:

$$-[O-CH_2-CH(CH_3)]_n-O- \quad (2)$$

R3 Aliphatic radical, e.g. $-(CH_2)_6-$ from diamine employed to extend the isocyanate prepolymer chain, built into the chain through applicable urea structures

The COO^{-} groups, which make principal elements of PU anionomers, are located in the element *R*, and they are derived in most cases from some additional substrates, e.g. dihydroxyacids:

$$(-O-CH_2)_2-C(CH_3)-COOH \quad (3)$$

but they can also be introduced in other locations within the PU chain—resulting from chemical modifications of that chain [2].

Yet, the actual structure of a PU chain can be much more complex, and it is dependent not only on the type of employed raw materials but also on the conditions adopted for the polyaddition process, e.g. which feedstocks were charged earlier and which were charged later, stoichiometry of reaction, process temperature and time, as well as the possible presence and amount of polyaddition catalyst used. The process conditions are responsible for the fact that PU macro-molecules can also comprise biuret groups, allophanate groups, carbodiimide or azaheterocyclic isocyanurate structures or oxazolidone structures. The majority of additionally created structures are polar in their nature. This adds to the nature of carboxyl, urethane and ether or ester groups, which are typical for anionomers. Hence, the polarity of resultant PUs becomes considerable and those materials offer better solubility in water (as compared to insoluble non-ionic PUs) and in polar organic solvents, e.g. *N*,*N*-dimethylacetamide, dimethylformamide (DMF) or acetonitrile dimethylsulphoxide. When a PU anionomer is not completely water-soluble, it is usually capable of forming aqueous emulsions or dispersions, and it can form specific polymer gels in the presence of organic solvents [3]. This should be accounted for by enhanced polar interactions of the dipole–dipole or dipole-induced dipole type and by ionic interactions in the polymer–solvent and polymer–polymer systems. Moreover, a higher tendency to form hydrogen bonds as compared to non-ionic PUs brings its contribution, too. It is for the above reasons that the molecular weight specifications of ionomers have to be analysed by the gel permeation chromatography (GPC) method with the use of polar solvents, while a medium-polarity eluent like tetrahydrofuran is a sufficiently good solvent for analysing linear PUs [4–6].

One can expect that such strong interactions between polar functional groups in PU anionomers will notably affect the supermolecular structure, arrangement of phases and separation of flexible and rigid segments present in PUs. These issues, in turn, are decisive for the electrical properties of PUs, resulting in improved conductivity and a higher dielectric constant of these materials. The surface energies of the anionomers considered can be modified by introducing functional groups and structural segments with hydrophobic (non-polar hydrogen groups and low-polarity ether groups) and hydrophilic (polar acid groups, amine groups and ammonium groups) performances [7]. PU elastomers, which have some features of ionomers, were found to offer improved thermal stability and improved mechanical properties, and even a higher potential for thermodynamic miscibility with non-polar polymers, e.g. poly(p-phenylene vinylene), or with polar polymers, e.g. poly(styrene-acrylic acid) [8, 9].

For the above reasons, PU ionomers have drawn the attention of numerous researchers since the 1980s [2, 10, 11]. The systems which contained carboxyl and sulpho groups were synthesised [12–16], and with carbon or fluorocarbon [17, 18] trunk chains. Recent literature reports confirm continual interest in this group of polymers, which are applicable, for example, as waterborne and environmentally friendly lacquers and adhesives wherein no additional emulsifiers are required [19–21]. These materials are even more interesting because the intermediates used for their manufacture—urethane–isocyanate prepolymers—are not water-compatible and they first need to be accurately reacted with polyols in the aqueous medium. Urethane–isocyanate anionomers, on the other hand, demonstrate the ability to react selectively in the aqueous medium with diamines, e.g. with 1,6-hexamethylenediamine. This process extends the PU chain but no hydrolysis of isocyanate and no release of CO_2 takes place, which is the case when foamed plastics are produced in situ [22, 23]. In case of classic linear PUs containing strongly hydrophilic urethane and hydroxyl groups, it is also possible to produce emulsions, but additional surfactants are required to make those emulsions stable, and the dispergation process becomes effective only after high shear rates are employed [24].

We employed PU anionomers in our previous research in the form of aqueous dispersions as the so-called temporary binders, which made it possible to mould the oxide-type ceramic materials into products [6]. Attempts were also made to evaluate the surface energies of so-produced aqueous dispersions [7].

Having in mind that the assessment of the extent of polar interactions in anionomers is critical for explaining the observed physical–chemical and mechanical properties, we launched a research programme intending to identify instrumental methods capable of evaluating the said properties in relation to the ionomer structure. This part of our study has been dedicated to just that issue. Based on our earlier knowledge in this field, we synthesised a number of anionomers that—at this stage of our research—had different structures of rigid urethane sections only. The different urethane groups resulted from different isocyanates employed. It is not meaningless for potential future applications that the type of diisocyanate used defines numerous performance properties of PUs, like the resistance of PU coatings to photo-degradation, the resistance to hydrolysis or biodegradability (still ranked low) which is important for the utilisation of wastes, e.g. spent PU foam.

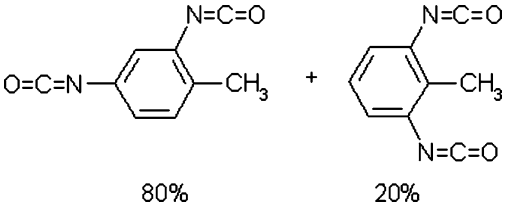
We plan to present the electrical and thermal properties in another part of our work, and to discuss them from the viewpoint of structural questions (described herein) and

structurally conditioned phase arrangement questions (not presented herein).

Experimental

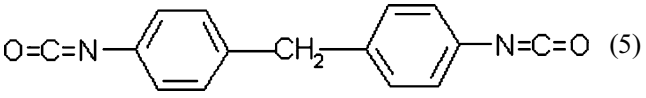
Raw materials and reagents

A technical product from Aldrich, 2,4- and 2,6-tolylene diisocyanate (TDI), was used in this study. This product was a mixture of 2,4-TDI and 2,6-TDI isomers, at percentages of 80 and 20 %, respectively. The reagent was used as purchased. The following structure illustrates the reagent:



(4)

The following structure illustrates the reagent 4, 4′-methylenebis(phenyl isocyanate) (MDI) from Aldrich. This reagent was used as purchased:

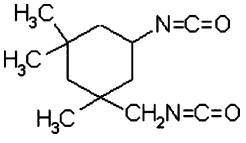


(5)

The following structure illustrates the reagent hexamethylene-1,6-diisocyanate (HDI) from Aldrich. This reagent was used as purchased:

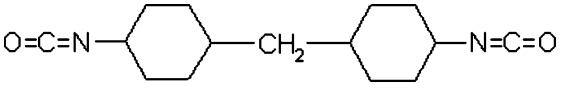
$$O = C = N(CH_2)_6N = C = O$$

The following structure illustrates the reagent isophorone diisocyanate [5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane] (IPDI) from Aldrich. This reagent was used as purchased:



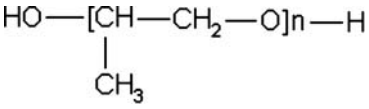
(6)

The following structure illustrates the reagent 4, 4′-methylenebis(cyclohexyl isocyanate) (HMDI) from Aldrich. This reagent was used as purchased:



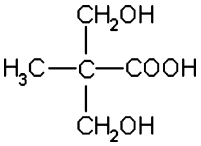
(7)

The following structure illustrates the reagent polyoxypropylene glycol (M_n=450 g/mol) (Rokopol 7P) from Chemical Factory “Rokita S.A.” in Brzeg Dolny (Poland) (this product was dried under vacuum in nitrogen at 120 °C for 2 h):



(8)

The following structure illustrates the reagent 2,2-bis (hydroxymethyl)propionic acid (DMPA) from Sigma Aldrich. This reagent has a melting point of 190 °C, and is a hygroscopic product. The reagent was dried directly before its use in a cabinet drier at 120 °C:



(9)

The following structure illustrates the reagent 1,6-hexamethylenediamine (HMDA) from Aldrich. The reagent was used as purchased:

$$H_2N(CH_2)_6NH_2 \quad (10)$$

The following structure illustrates the reagent triethylamine (TEA) from POCh Gliwice S.A., Poland. The reagent was used as purchased:

$$N(CH_2 - CH_3)_3 \quad (11)$$

Diazabicyclo-[2,2,2]-octane (DABCO) from Aldrich was used as the catalyst in the production of urethane–isocyanate prepolymers. Tetrahydrofuran and DMF were supplied by POCh Gliwice S.A., Poland. These solvents were purified by distillation.

Method for the synthesis of urethane anionomers

To produce urethane anionomers, the step-growth polyaddition method, which was developed earlier, was employed [4]. This method is based on obtaining the urethane–isocyanate prepolymer from a selected pair of diisocyanate and polyol at the first stage. At further steps, this prepolymer is reacted with DMPA, and, finally, its COO^- groups are neutralised with TEA, and the prepolymer chain is extended in the aqueous dispersion medium with 1,6-hexamethylenediamine. What was critical for the adopted synthesis method was to provide adequate molar ratios for the introduced reacting substances at successive reaction stages. All the synthesis processes were carried out in a glass stand, i.e. in a three-necked flask provided with a magnetic stirrer, a dropping funnel, a thermometer, a reflux condenser and a nitrogen supply point.

Table 1 Conditions for synthesis of PU anionomers

Sample no.	Stage no.	Type of diisocyanate	Type of polyol	Type of ionogenic reactant	Content of –NCO groups (wt. %)		Type of extension agent	Molar ratio of groups –NCO to –OH	Dry matter content (wt. %)
					Theoretical	Experimental			
1	1	Synthesis of isocyanate prepolymer (T=80 °C, t=20 min)			10.52	9.90	–	2:1	–
		TDI	Rokopol 7P (M=450)	–					
	2	Synthesis of isocyanate ionomer (T=60 °C, t=20 min)			2.72	2.30	–	2:1	–
		–		DMPA					
		Neutralisation of ionomer by means of TEA (T=20 °C, t=15 min, pH 7.5)							
	3	Extension of isocyanate ionomer and emulsification in water (T=20 °C, t=20 min)					HMDA	1:1	20.0
	4	Evaporation of solvents from emulsion and formation of coating (T=110 °C, t=60 min)							
2	1	Synthesis of isocyanate prepolymer catalyst DABCO (0.1 wt. %) (T=30 °C, t=20 min)			5.09	3.50	–	3:2	–
		MDI	Rokopol 7P (M=450)	–			–		
	2	Synthesis of isocyanate ionomer (T=50 °C, t=60 min)			2.44	1.19	–	2:1	–
		–		DMPA					
		Neutralisation of ionomer by means of TEA (T=20 °C, t=15 min, pH 7.5)							
	3	Extension of isocyanate ionomer and emulsification in water (T=20 °C, t=60 min)					HMDA	1:1	27.0
	4	Evaporation of solvents from emulsion and formation of coating (T=110 °C, t=60 min)							
3	1	Synthesis of isocyanate prepolymer catalyst DABCO (0.1 wt. %) (T=100 °C, t=40 min)			4.98	6.60	–	3:2	–
		HMDI	Rokopol 7P (M=450)	–					
	2	Synthesis of isocyanate ionomer (T=80 °C, t=30 min)			2.39	2.00	–	2:1	–
		–		DMPA					
		Neutralisation of ionomer by means of TEA (T=80 °C, t=10 min, pH 7.5)							
	3	Extension of isocyanate ionomer and emulsification in water T=80 °C, t=30 min					HMDA	1:1	22.0
	4	Evaporation of solvents from emulsion and formation of coating (T=110 °C, t=60 min)							

Table 1 (continued)

Sample no.	Stage no.	Type of diisocyanate	Type of polyol	Type of ionogenic reactant	Content of –NCO groups (wt. %)		Type of extension agent	Molar ratio of groups –NCO to –OH	Dry matter content (wt. %)
					Theoretical	Experimental			
4	1	Synthesis of isocyanate prepolymer catalyst DABCO (0.5 wt. %) (T=90 °C, t=120 min)			5.36	4.30	–	3:2	–
		IPDI	Rokopol 7P (M=450)	–					
	2	Synthesis of isocyanate ionomer (T=80 °C, t=30 min)			2.57	1.80	–	2:1	–
		–		DMPA					
		Neutralisation of ionomer by means of TEA (T=80 °C, t=10 min, pH 7.5)							
	3	Extension of isocyanate ionomer and emulsification in water (T=70 °C, t=30 min)					HMDA	1:1	24.0
	4	Evaporation of solvents from emulsion and formation of coating (T=110 °C, t=60 min)							
5	1	Synthesis of isocyanate prepolymer (T=100 °C, t=90 min)			5.98	6.0	–	3:2	–
		HDI	Rokopol 7P (M=450)	–					
	2	Synthesis of isocyanate ionomer (T=100 °C, t=30 min)			2.85	1.8	–	2:1	–
		–		DMPA					
		Neutralisation of ionomer by means of TEA (T=80 °C, t=10 min, pH 7.5)							
	3	Extension of isocyanate ionomer and emulsification in water (T=80 °C, t=30 min)					HMDA	1:1	26.0
	4	Evaporation of solvents from emulsion and formation of coating (T=110 °C, t=60 min)							

Stage 1—synthesis of isocyanate prepolymer (AB_2)

Urethane–isocyanate prepolymer was obtained by adding molten Rokopol 7P drop by drop to the flask, where successively selected diisocyanates had been previously placed. The temperature of the Rokopol was maintained at 30–100 °C by means of an IR radiator. In case of MDI and HMDI diisocyanates, the reactions were conducted in the presence of the DABCO catalyst. The specific conditions for individual reactions are detailed in Table 1. This stage can be illustrated as follows:

The dropwise addition of Rokopol 7P at 60 °C took 20 min. The resulting mixture was then maintained at 75 °C over 60 min, under a reflux condenser and dry nitrogen. After the reaction was completed, the mixture was cooled down to 50 °C. The content of –NCO groups was then determined by a generally known method based on dibutylamine [26], and the findings were compared to the expected value—calculated from the adopted stoichiometry (Table 1). The experimental values were usually somewhat lower, which can be explained by too-high conversion of small amounts of initially formed trimers

$$\begin{array}{ccccc} \mathrm{HO\text{-}A\text{-}OH} & + & \mathrm{2\ OCN\text{-}B\text{-}NCO} & \longrightarrow & \mathrm{OCN\text{-}B\text{-}NH\text{-}CO\text{-}O\text{-}A\text{-}O\text{-}CO\text{-}NH\text{-}B\text{-}NCO} \\ \mathrm{(A)} & + & \mathrm{(B)} & \longrightarrow & \mathrm{(AB_2)} \end{array} \quad (12)$$

where A is the segment derived from Rokopol 7P structure Eq. (8) and B is the segment derived from the diisocyanate structure.

AB_2 with, for example, temporarily present tetramers A_2B_2 to prepolymers A_3B_4 with higher molecular weights, as presented in previous reports [4, 25].

Stage 2—synthesis of urethane–isocyanate anionomer and its ammonium salt

Urethane–isocyanate anionomer, which contained –COOH groups, was synthesised with the use of DMPA (X) as a chain extender for the AB_2 prepolymer:

$$2\ AB_2 + X \rightarrow BABYBAB \tag{13}$$

where X is DMPA Eq. (9) and Y is a segment derived from built-in DMPA.

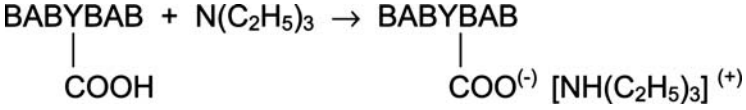
DMPA was added to the reactor in the form of solution in DMF (1:7). The reaction was continued at 50–100 °C over 20–60 min, and then the concentration of –NCO groups was checked again and compared to the theoretical value (Table 1). Afterwards, the urethane–isocyanate macro-anionomer (UAMA) (with the carboxyl groups in its structure) was subjected to the reaction (structural fragment Y) with TEA, which yielded the triethylammonium cation. That reaction can be represented by the following equation:

The macro-anionomer produced in this way was capable of forming aqueous dispersions. The obtained UAMA with the number of –COOH groups known from stoichiometric calculations was reacted with the equimolar amount of TEA. The amine was added at 20–80 °C until the level of pH 7.5 was reached.

In these conditions, the free –NCO groups of this macro-anionomer react much slower with the carboxylate groups than with water and $–NH_2$ groups coming from HMDA amine, which was put in during stage 3. Therefore, the additional creation of the possible amide crosslinkings with the part of $–COO^-$ groups which are present in the segments coming from DMPA can be neglected.

Stage 3—extension of urethane macro-anionomer in the reaction with 1,6-hexamethylenediamine

The Urethane–isocyanate anionomers left unconverted from stage 2 were then extended by means of HMDA.



(14)

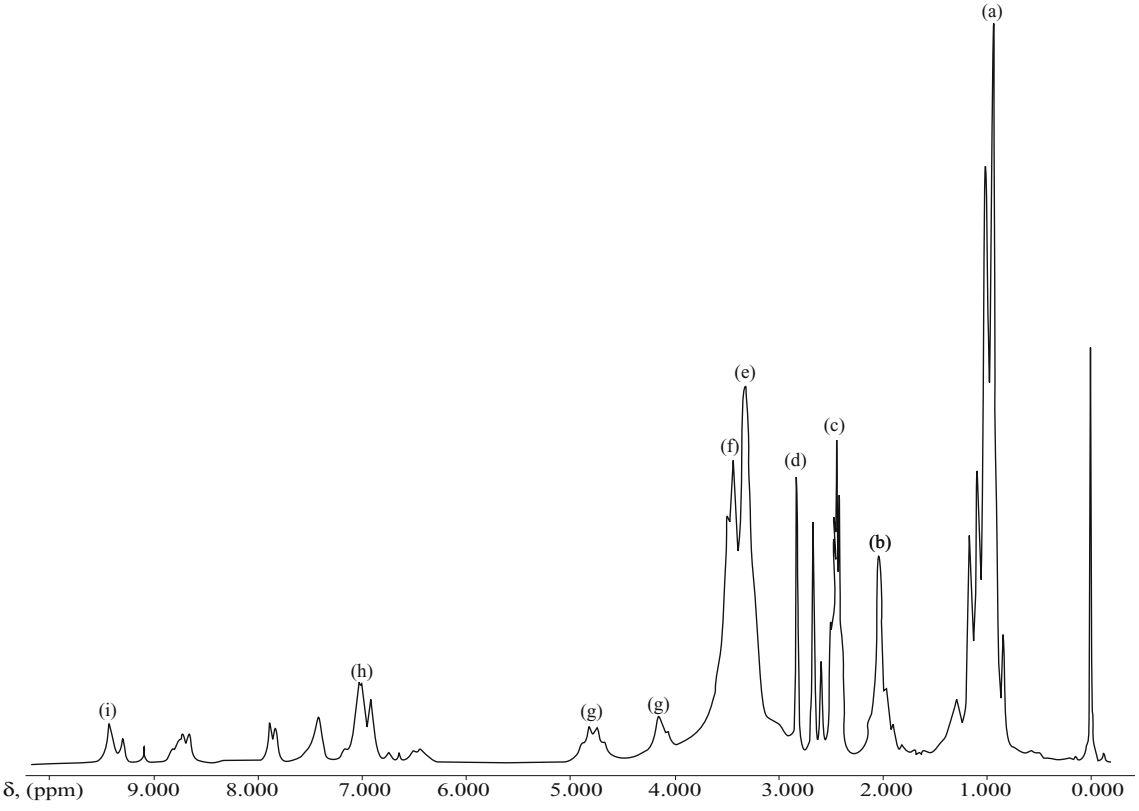
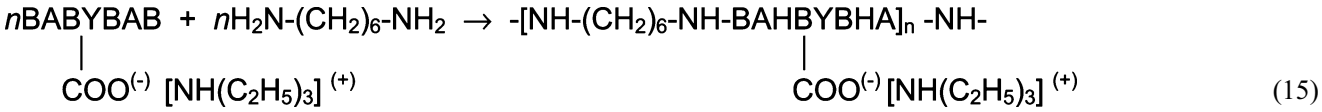


Fig. 1 NMR spectrum of anionomer no. 1, based on TDI isocyanate

The reaction was carried out in aqueous dispersion, taking advantage of higher reactivity of isocyanate groups with amino groups in water:



(15)

The major amount of HMDA (90 %) was added in the form of solution in tetrahydrofolate (THF) at room temperature. The mixture was then subjected to mechanical dispergation for another 30 min at room temperature: intense agitation was applied with the dropwise addition of re-distilled water. THF was subsequently recovered from the obtained emulsion by means of distillation. The dry matter content (wt. %) in the produced aqueous–THF–DMF emulsion was determined by gravimetric analysis after evaporation of the solvents in a drier at 120 °C over 120 min (Table 1).

Stage 4—evaporation of solvents from emulsions and formation of films

Aqueous emulsions of produced anionomers were placed in a drier (T=110 °C, t=60 min). After the evaporation of water, polymer films were produced which were used in further investigations.

Testing equipment and analytical methods

Determination of –NCO group content

The determination of –NCO group content involved a well-known method, and dibutylamine was used in the tests. The excess of unreacted amine was titrated with the HCl solution and bromophenol blue was used as an indicator [26].

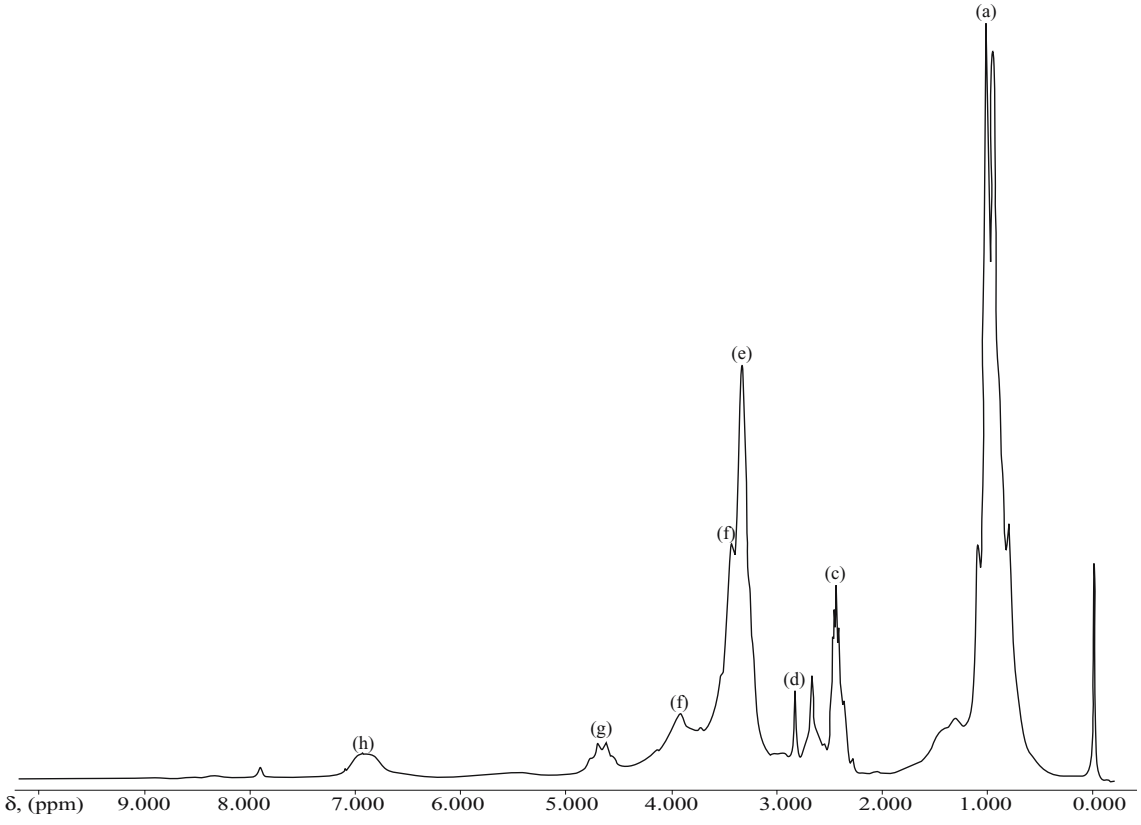


Fig. 2 NMR spectrum of anionomer no. 3, based on IPDI isocyanate

Table 2 Interpretation of ^{1}H-NMR spectra for synthesised anionomers

Sample №	Group of signals δ (ppm)	Type of protons	Symbol of signal in Fig. 1 and 2	Origin of structural fragment
1-5	0.8-1.7	N-(CH$_2$-**CH$_3$**)$_3$ -O-(-CH$_2$- CH- O-)$_n$- | **CH$_3$** -NH- CH$_2$-**(CH$_2$)$_4$**-CH$_2$-NH-CO-	(a)	TEA ROKOPOl 7P HMDA
5		**CH$_3$**-C(CH$_2$-OH)$_2$COOH		DMPA
		-CO-NH-CH$_2$-**(CH$_2$)$_4$**-NH-CO-		HDI
1	2.04	**CH$_3$**-Ar	(b)	2,4- and 2,6-TDI
1-5	2.44	**(CH$_3$)$_2$**SO	(c)	solvent (h$_6$DMSO)
1-5	2.5-2.9 (multiplet)	N-(**CH$_2$**-CH$_3$)$_3$ -HN-**CH$_2$**-(CH$_2$)$_4$- **CH$_2$**-NH- CH$_3$-C(**CH$_2$**-OH)$_2$COOH	(d)	TEA HMDA, HDI DMPA
1-5	3.3 s	(CH$_2$-CH$_3$)$_3$N**H**$^+$ COO$^-$	(e)	TEA
1-5	3.4-3.8	-O-(-**CH$_2$**- **CH**- O-)$_n$- | CH$_3$ NH$^+$-(**CH$_2$**-CH$_3$)$_3$	(f)	Rokopol 7P Protone TEA
1-5	3.94-4.29 (multiplet)	-urethane-NH-CO-O-**CH$_2$**- -urethane-NH-CO-O-**CH**- (-urethane-NH-CO-O-**CH$_2$**)$_2$-C-CH$_3$) | COO$^-$ -urethane-NH-CO-NH-**CH$_2$**-(CH$_2$)$_4$-	(g)	isocyanate+ Rokopol 7P isocyanate+DMPA TDI+HMDA isocyanate+HMDA
1,2	6.9-7.1 (multiplet)	**-CH-** Ar	(h)	2,4- and 2,6-TDI and MDI
1	> 9	-R-**NH**-CO-O-	(i)	Urethane from isocyanate

High-resolution nuclear magnetic resonance (^{1}H-NMR) spectroscopy

High-resolution nuclear magnetic resonance (^{1}H-NMR) spectra of the obtained polymers were taken with the use of a FT NMR 80 MHz spectrometer (Tesla 587A). The samples of coating (i.e. produced anionomers) were dissolved in DMSO-d$_6$/h-DMSO, and the solutions with concentrations of about 0.2 g/dm^3 were prepared. Hexamethylenedisiloxane made a standard.

IR spectroscopy

IR spectra were taken with the spectrophotometer Paragon 1000 FT-IR, within 4,000–6,500 cm^{-1}, with the use of the attenuated total reflection technique (the polymer film was placed between the prism walls. The obtained spectra were presented as the relation of transmittance [%] vs wave number $\overline{\nu}$ [cm^{-1}]).

Gel permeation chromatography (GPC)

The size exclusion chromatography analyses of PU polymers were performed using a modular high-performance liquid chromatography, pump type HPP 5001 (Laboratorni Pristroje, Czech Republic), column 500×8 mm, GM 1000 (Labio, Czech Republic), filled with a polymethacrylate sorbent (10 μm), RIDK 101 refractive index detector (ECOM, Czech Republic), and with *N*,*N*-dimethylacetamide +0.5 wt. % LiBr as a mobile phase (flow rate of 1 cm^3/min), temperature of 25 °C, sampling volume of 20 μl and concentration of the sample of 10 mg/cm^3. For the data collection and treatment, CSW 1.7 and Clarity GPC software (DataApex, Czech Republic) were used. The system was calibrated by means of narrow molecular weight polystyrene standards. The equation of calibration curve was:

$$Y = -0.41809\,X + 9,86939\ (CorrelationFactor:\ 0.9870788) \tag{16}$$

Results and discussion

Chemical structure and polarity nature of anionomers

Figures 1 and 2 show the exemplary ^{1}H-NMR spectra of aromatic anionomer no. 1, which was synthesised with the use of TDI, and that of anionomer no. 4, which was obtained with the use of cycloaliphatic diisocyanate IPDI. Table 2 presents interpretations for NMR spectra for all anionomers; the individual signals (*a*–*i*) have been linked to the corresponding protons. The obtained spectra confirm, in general, the expected structures, and at the same time they reveal, for example in sample no. 4, the presence of residual aromatic protons, which have probably been introduced by incompletely purified diisocyanate IPDI.

Based on the relative integration of individual signals in the recorded spectra, the attempt was made to evaluate the polarities of the chemical structures of the tested anionomers. For that purpose, the integration ratio was calculated as:

$$\kappa_1 = \frac{I_P}{I_P + I_N} \tag{17}$$

for the signals representing protons in groups CH_2 and CH connected to polar ether, amino and urethane groups, located in a wide band of δ=2.5–4.3 ppm (I_P) (signals designated *d*, *e*, *f* and *g*), referred to total integration of I_P and I_N, where I_N means the integration of signals derived from protons of non-polar alkyl groups (CH_3– and –CH_2–) (signals designated *a* and *b*) (I_N) located within the band δ=0.8–2.2 ppm:

$$I_N = \sum_{i=27}^{37} I_i \tag{18}$$

where *i* represents the successive signals within δ=0.8–2.2 ppm

$$I_P = \sum_{i=27}^{37} I_j \tag{19}$$

where *i* represents the successive signals within δ=2.5–4.3 ppm, where, for the spectra of aromatic anionomer samples no. 1 and 2, the following value was calculated:

$$\kappa_2 = \frac{I_P}{I_P + I_N + I_A} \tag{20}$$

to take additionally into consideration the integration I_A for signals representing aromatic protons (*h*) which bring their contributions to non-polar structures:

$$I_A = \sum_{i=4}^{9} I_k \tag{21}$$

where *i* represents the signals within δ=6.9–7.1 ppm.

Thus, the κ_1 and κ_2 parameters defined by relationships Eqs. (17) and (20) describe, in the physical way, the molar part of the polar structures which are present in non-aromatic (no. 3, 4 and 5) and in aromatic (no. 1 and 2) anionomers.

The findings from the calculations are presented in Table 3. As results from these calculations and from the adopted criteria, anionomer no. 5, synthesised with the use of HDI, was found to be the most polar polymer (with the highest value of κ_1), the least polar structures were found to be anionomers no. 4 and 3 synthesised from diisocyanates IPDI and HMDI, respectively, while the aromatic anionomers no. 1 and 2 turned out medium-polar.

Table 3 Structural features of synthesised PU anionomers

Sample no.	Type of diisocyanate	Analysis of NMR spectra								Analysis of IR spectra				
		Signals in NMR spectra	I_N (relative scale)	Signals in NMR spectra	I_P (relative scale)	Signals in NMR spectra	I_A (relative scale)	κ_1	κ_2	A_{1700} (relative scale)	A_{1550} (relative scale)	A_{2900} (relative scale)	κ_3	κ_4
1	TDI	$I_N = \sum_{i=24}^{32} I_i$	34920	$I_P = \sum_{i=10}^{18} I_i$	33549	$I_A = \sum_{i=4}^{9} I_i$	3172	–	0.468	0.463	0.638	0.473	0.98	1.35
2	MDI	$I_N = \sum_{i=23}^{28} I_i$	27495	$I_P = \sum_{i=10}^{18} I_i$	36247	$I_A = \sum_{i=3}^{9} I_i$	9669	–	0.494	0.595	0.752	0.589	1.01	1.28
3	HMDI	$I_N = \sum_{i=32}^{40} I_i$	38780	$I_P = \sum_{i=8}^{23} I_i$	29996	–	0	0.436	–	0.552	0.710	1.894	0.29	0.37
4	IPDI	$I_N = \sum_{i=15}^{21} I_i$	64818	$I_P = \sum_{i=1}^{9} I_i$	45976	–	0	0.415	–	0.632	0.533	0.870	0.73	0.62
5	HDI	$I_N = \sum_{i=27}^{37} I_i$	45555	$I_P = \sum_{i=5}^{21} I_i$	49615	–	0	0.521	–	0.767	0.632	1.105	0.69	0.57

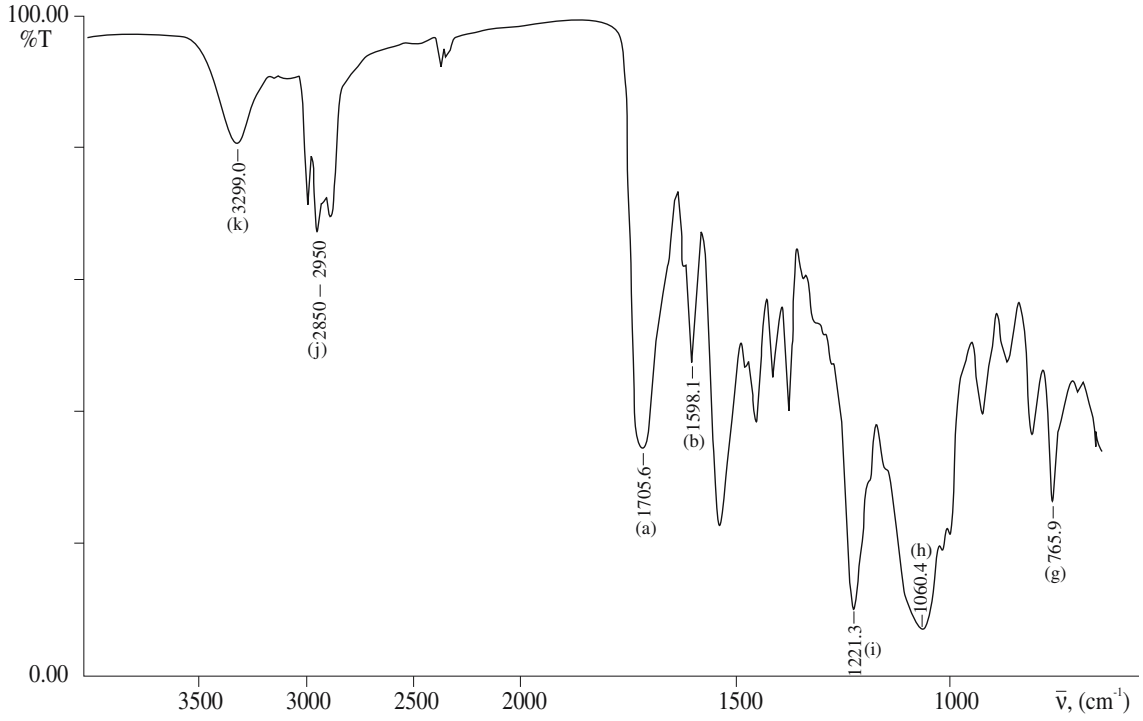


Fig. 3 IR spectrum of anionomer no. 1, based on TDI isocyanate

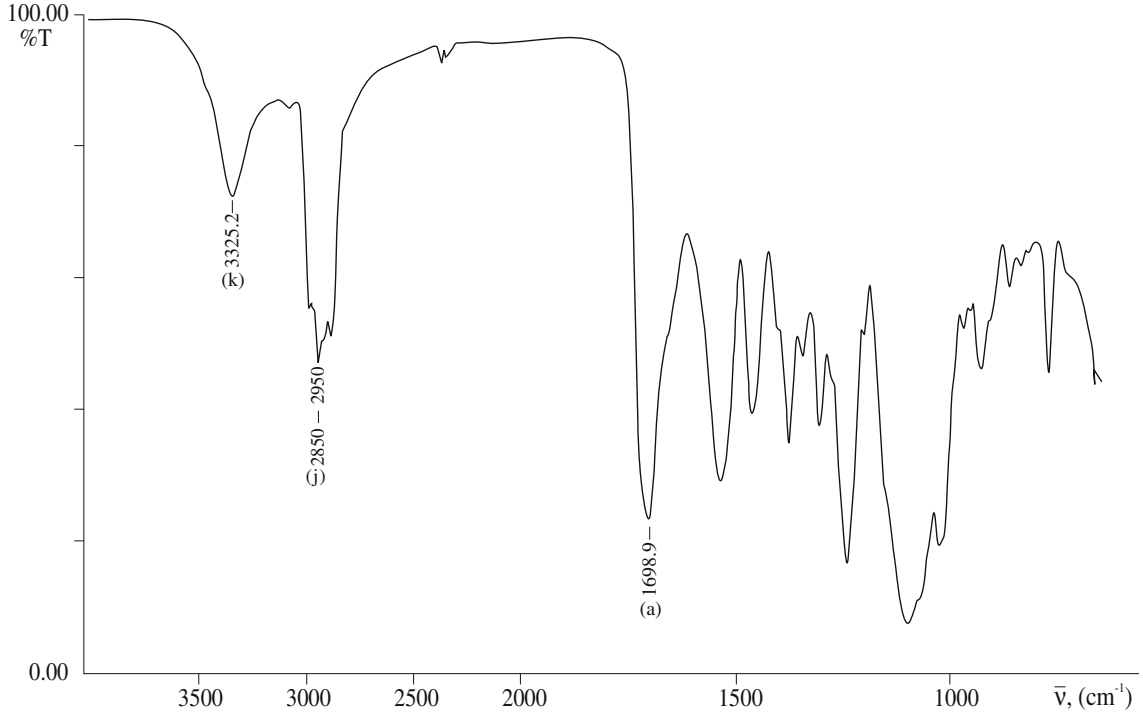


Fig. 4 IR spectrum of anionomer no. 3, based on TDI isocyanate

The supplementary structural information was obtained by analysing the IR spectra of the studied anionomers, which also confirmed the presence of PU-type structures. Figure 3 presents the example of the IR spectrum of aromatic anionomer no. 1, while Fig. 4 shows the spectrum of cycloaliphatic anionomer no. 4. The bands at about 1,599 and 1,618 cm^{-1} are present in the spectra of anionomers no. 1 and 2 only—these represent the in-plane skeletal vibrations of the aromatic ring.

The bands at about 1,730 and 3,300 cm^{-1}, recorded in all spectra, correspond to the stretching vibrations of the carbonyl group =**C**=**O** (the so-called first amide band) and of the imine group –**NH**–, respectively, forming the urethane segment –**NHCOO**–. The shift of the carbonyl band towards lower frequencies (1,706 and 1,700 cm^{-1}) for all the studied anionomers gives rise to the evidence for numerous intra-molecular and extra-molecular hydrogen bonds which involve the group =**C**=**O**. The band representing the combinative deformation vibrations—scissoring vibrations of **N**–**H** and stretching vibrations of **C**–**N**—can be observed within about 1,550 cm^{-1}, as expected. That region is specific for the so-called second amide band, which is always present for PUs.

The so-called fifth band of the group **N**–**H** is present at 766 cm^{-1}—it is clearly visible in aromatic anionomers no. 1 and 2. Within 1,000–1,300 cm^{-1}, a group of very wide and intense bands, which correspond to stretching and asymmetric vibrations of the ether group **C**–**O**–**C** in the ether-urethanes, formed (1,060 cm^{-1}).

The bands located at about 1,220 cm^{-1} are not specific here because they can result from stretching vibrations of **C**–**O** and **O**–**CO** in urethanes, from vibrations of **C**–**H** in urea derivatives of aliphatic amines TEA and HMDA, from wagging and twisting deformation vibrations of **C**–**H** in methylene groups, from deformation vibrations of **C**–**H** in the TDI ring plane and from stretching vibrations of **C**–**N** (so-called third amide band).

The band at 2,270 cm^{-1}, for asymmetric stretching vibrations of the group –**NCO**, is the most specific band for isocyanates and it was observed only in the case of urethane–isocyanate prepolymers obtained at stages 1 and 2 (Table 1). Within 2,850–2,950 cm^{-1} (j), the bands are present for stretching vibrations, both symmetric and asymmetric, of **C**–**H** alkyl groups which can be found in the structures of Rokopol 7P, DMPA and created urethanes. Because considerable amounts of alkyl groups are present in every studied polymer, that band can be assumed to make the reference band for the intensity figures of other bands in the analysed spectra.

The expected presence of the ionic group of PU anionomer can be evidenced by the band at about 1,450 cm^{-1} (Fig. 3) for the group –$\mathbf{CH_2}$–**N**<, while the band for $\mathbf{N^+}$–**H** in the tertiary amine (TEA) salt is usually low in intensity, and it is probably for this reason that this band cannot be observed.

The ratios of absorbances at bands for stretching vibrations of group **C**=**O**, 1,680–1,720 cm^{-1} (A_{1700}), and for deformation vibrations of **N**–**H** (A_{1550}) in urethane groups, 1,550–1,500 cm^{-1}, to absorbances at bands for valency vibrations of **C**–**H** in alkyl groups, 3,000–2,800 cm^{-1} (A_{2900}), calculated from the recorded IR spectra are as follows:

$$\kappa_3 = \frac{A_{1700}}{A_{2900}} \quad \kappa_4 = \frac{A_{1550}}{A_{2900}} \tag{22}$$

These ratios were assumed to make the additional and independent criterion for the evaluation of the polarity of the chemical structures in synthesised anionomers.

The higher the values of the κ_3 and κ_4 parameters are, the higher the contribution to chemical interactions that should be expected from polar urethane groups which are present in macro-molecules of synthesised anionomers is. This results not only from the higher polarity of these groups but also from their higher average molecular weights—which we are going to prove in the later part hereof. As results from the data provided in Table 3, when just this criterion is considered, the highest share of urethane groups can be attributed to aromatic anionomers no. 1 and 2. A comparable share of urethane groups can be found in anionomers no. 4 and 5, while the lowest share is typical for anionomer no. 3. The values of the κ_3 and κ_4 parameters (Table 4) obtained on the basis of IR spectra correlate with the κ_1 and κ_2 values (Table 3) obtained from NMR spectra only to some extent. The additional valuable information comes from the GPC analysis of molecular weights of synthesised anionomer macro-molecules.

Table 4 Interpretation for GPC chromatograms of synthesised anionomers

Sample no.	Type of diisocyanate	Max RT (min)	Start RT (min)	End RT (min)	M_p (g/mol)	M_n (g/mol)	M_w (g/mol)	PD	M_1	n	k (wt. %)
1	TDI	13.34	10.41	16.94	19653	10852	41816	3.85	1948	21.47	2.26
2	MDI	13.25	9.81	16.40	21432	13177	39470	3.00	2252	17.53	1.95
3	HMDI	14.34	12.19	17.31	7457	4255	7939	1.87	2301	3.45	1.91
4	IPDI	14.13	11.53	16.84	9157	6300	12823	2.04	2141	5.99	2.06
5	HDI	13.81	11.28	16.42	12501	8441	18331	2.17	1924	9.53	2.29

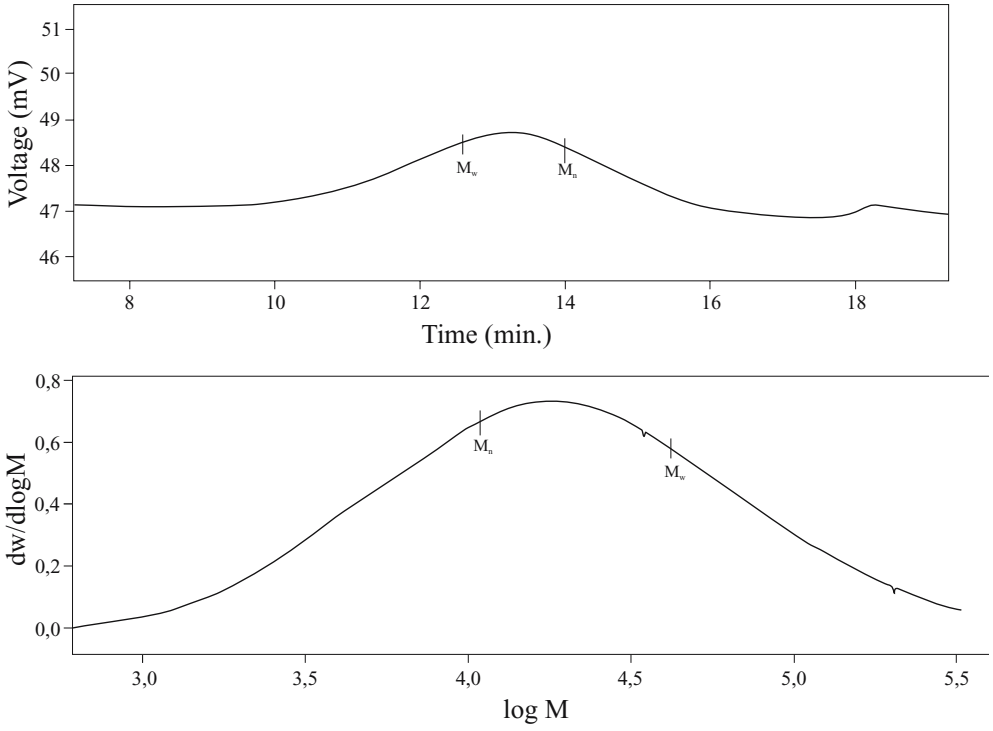


Fig. 5 GPC chromatogram of anionomer no. 1

Effect of molecular weight on the polarity of synthesised anionomers

Figure 5 provides an example of the GPC chromatogram for anionomer no. 1, while Fig. 6 presents the molecular weight distribution (MWD) differential curves for all synthesised anionomers obtained from the chromatograms (which were taken earlier) and the adopted calibration Eq. (16). The details from the GPC analyses [maximum of retention peak; maximum retention time (RT); start RT; end RT; average molecular weights: M_p, M_n, M_w, and polydispersity (PD)] of the studied anionomers are presented in Table 4.

As results from those data, anionomers with much different average molecular weights and PD within anionomers no. 2–4 were produced, despite the fact that nearly identical multi-step synthesis methods were employed. The highest values of molecular weights are offered by anionomers no. 1 and 2 ($M_w \cong 40{,}000$), while the molecular weight of anionomer no. 3, obtained from

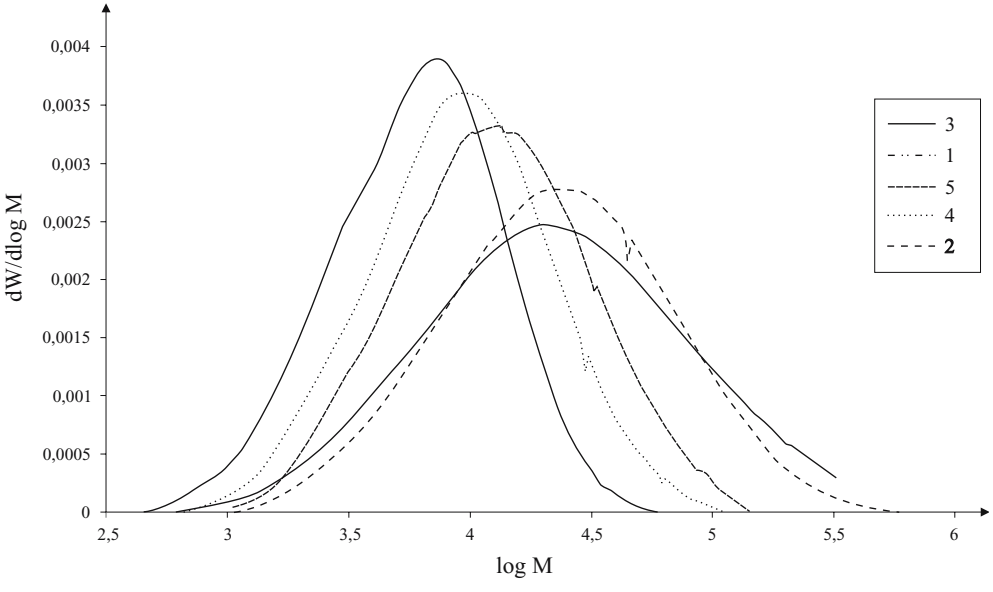


Fig. 6 Differential MWD curves of anionomers no. 1–5

HMDI, is much lower, and it only reaches $M_w \cong 8{,}000$. These differences should be accounted for by much lower chemical reactivity of cycloaliphatic diisocyanates HMDI and IPDI, and different "chemical values" of both their –NCO groups. Moreover, different parameters adopted for the synthesis process (temperature, time of reaction and presence of DABCO catalyst) are responsible—these parameters were selected predominantly to produce stable intermediates applicable in further steps of the synthesis. What is additionally essential is the fact that, for example, aliphatic HDI has two –NCO groups in its molecule which offer chemical "equal values". Hence, the molecule is likely to grow equally in both directions, and despite lower chemical activity than that of MDI, the use of HDI made it possible to produce anionomers with $M_w \cong 18{,}000$ g/mol.

Column 10 in Table 4 provides additional molecular weights for hypothetically repeated structural units M_1 in the synthesised anionomers

$$BABYBAB(TEA)(HMDA) \tag{23}$$

calculated from the expected chain structure Eq. (1), with due consideration of structural segments derived from individual parent substances that reacted in accordance with the assumed reaction stoichiometry Eqs. (12, 13, 14 and 15).

Column 11 in Table 4 specifies the values for the factor

$$n = \frac{M_w}{M_1} \tag{24}$$

which represents the statistical amount of monomeric units M_1 in the chains of individual anionomers, identified with their polymerisation degree, which is defined analogically as for the chain-growth polymerisation. Thus, the calculated value of n should be correlated to the parameters κ_3 and κ_4, as found on the basis of IR spectra (Table 3), because this calculated value is proportional (i.e. twice as high on average) to the number of urethane groups in individual anionomer macro-molecules. As is visible, this conformity really takes place for anionomers 1, 2 and 5, while for anionomers no. 4 and 5, this sequence is changed, which probably results from inaccuracies in the calculations, because the difference between the parameters κ_3 and κ_4 turned out to be small for those anionomers. Hence, the factor n calculated on the basis of GPC measurements, which is more diversified, seems to make a more convenient measure for the polar interactions resulting from the presence of urethane groups in anionomers no. 4 and 5. With regard to aromatic anionomers no. 1 and 2 and their GPC findings, their κ_4 parameters seem more credible than the κ_3 parameters, as the κ_4 parameters provide better correlation with the values of n.

The obtained findings can now be set up against the values of parameters κ_1 and κ_2, which provide a more general characterisation of polarity. Polarity is affected not only by urethane groups but also by other functional groups, e.g. those derived from primary and tertiary amines (HMDA, TEA) used in the synthesis, those derived from ammonium ions formed by amines, DMPA-derived carboxyl groups and/or ether groups of Rokopol 7P. The effects of these functional groups on the polarity of the whole molecule were taken into consideration more carefully when analysing NMR spectra—these were visualised by the intensity of the signals representing the groups CH_2 within the band δ=2.5–4.3 ppm, said CH_2 groups being located in the position α to the polar groups in question. Having the above in mind, one can assume that the polarity of the studied anionomers increases as follows:

$$\begin{aligned} Anionomer5(HDI) &> Anionomer1(MDI) \\ &> Anionomer2(TDI) > \\ &> Anionomer3(HMDI) \\ &> Anionomer4(IPDI) \end{aligned} \tag{25}$$

It appears that the above sequence is much less affected by the content of ions COO^-—these ions' molar shares correspond to the polymerisation degree n (one group COO^- is present in the structural unit M_1). The weight share for groups COO^- was calculated from the formula:

$$k = \frac{n \cdot M_{COO^-}}{M_w} \cdot 100\% \tag{26}$$

where

n	The average polymerisation degree calculated from the formula (12)
$M_{COO^-} = 44$	The gram-equivalent of carboxyl group
M_w	The weight-average molecular weight, as found by the GPC method (Table 4)

As can be seen from the data presented in Table 4, the weight share for groups COO^- is nearly the same and close to about 2 wt. % for all the analysed anionomers.

Conclusions

When diisocyanates with various chemical structures are used and when suitable conditions are selected for successive polyaddition stages, it is possible—on the basis of a selected polyol-type component (polyoxypropylene glycol, in this case) and an ionogenic compound (DMPA)—to synthesise PU anionomers with nearly the same contents of ionic groups (about 2 wt. %), yet much different amounts of polar structures, which result from the presence of urethane groups, ether groups, carboxyl groups, amine groups and ammonium groups. The obtained anionomers turned out to be completely soluble in *N*,*N*-dimethylacetamide, which made it possible to determine their molecular weights and MWDs. The GPC

method together with IR and NMR spectroscopic methods made it possible to provide coherent structural characteristics for those polymers, principally from the viewpoint of their polarity specifications.

Numerous intra-molecular and extra-molecular interactions should result from the presence of the above-discussed polar structural components in the studied PU anionomers. One can expect those interactions to be responsible for diversified morphology of condensed phases in those anionomers, e.g. in the form of thin polymer coatings obtained by the conservative evaporation of aqueous dispersions. Moreover, the interactions are expected to yield unique mechanical, thermal, electric and surface properties of elastomer materials produced from those anionomers. This will make it possible to suggest new applications for such elastomers. We plan to dedicate part II of our paper to some of these issues.

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