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ORIGINAL CONTRIBUTION

Chemical structure and surface properties of the polyurethane cationomers

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Abstract Polyurethane cationomers were synthesised in the reaction of various diisocyanates with polyoxypropylene glycol and two *N*-alkyldiethanolamines. The obtained isocyanate prepolymers were then extended in the aqueous medium by means of 1,6-hexamethylenediamine; stable aqueous dispersions were thus obtained, which were applied to and distributed over the poly(tetrafluoroethylene) surface. After evaporation of water from those dispersions, thin polymer coatings were produced. The analyses with the use of ^{1}H, carbon-13 nuclear magnetic resonance and infrared spectroscopy methods confirmed chemical structures of synthesised cationomers. Also, attempts were made to quantitatively characterise polarities of those structures by means of factors that were defined especially for that purpose. Moreover, the physical model of van Oss–Good and wetting angles for coatings obtained from the polyurethane cationomers in question, measured with the use of standard liquids with various polarity specifications, were utilised to determine the surface free energy values for the obtained ionomers.

Keywords Polarity of bonds · ^{1}H and C^{13} NMR · IR spectroscopy · Surface free energy parameters

Introduction

Our earlier papers presented the synthesis methods, chemical structures and some selected—important from the viewpoint of application(s)—physical properties of polyurethane anionomers [1–3]. Polyurethane cationomers offer the properties that are not any less interesting and that result from even wider variety of chemical structures, as specific for linear polyurethanes. That question is worthy of considering, the more so because the latest reports pay much less attention to polyurethane cationomers than to polyurethane anionomers, although the former can offer—as we are going to present in this paper—new applicability as the so-called intelligent materials for which far-reaching changes in physical properties (electrical, optical and surface properties) are possible, depending on structural modifications. That subject was already discussed in our earlier papers [4, 5] in which the manufacturing method, structure and properties were presented for polyurethane cationomers obtained from 2,4- and 2,6-tolylene diisocyanate (2,4- and 2,6-TDI) or 4,4′-methylenebis(phenyl isocyanate) (MDI), from selected polyether polyols or polyester polyols and from difunctional tertiary amines, e.g. *N*-methyl or *N*-butyldiethanoloamine, which were incorporated into chains and reacted with formic acid to yield stable alkylammonium cations. Thus, obtained cationomers in the form of aqueous dispersions were employed as polyurethane lacquer coatings. Those applications have long been mentioned in research reports, but in our opinion, the results obtained so far are not so satisfactory as those for polyurethane anionomers [6, 7]. Aqueous polyurethane cationomers were produced also in a multi-stage poly-addition process of hexamethylene-1,6-diisocyanate (HDI), poly(oxypropylene) diol (M=400 g/mol) and *N*-methyldiethanoloamine (*N*-MDEA) as an ionogenic compound and isocyanate–urethane prepolymer chain extender at the same time. The obtained linear polyurethane was converted to cationomer in the quarternisation reaction of amino groups with dimethyl sulphate (VI), acetic acid or hydrochloric acid [8]. Some

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Schiff bases, like 2-chloromethyl-*N*-(2-hydroxybenzilidene) aniline, 3-(11-bromoundecanoyloxymethyl)-*N*-(2-hydroxybenzilidene) aniline and 4-chloromethylphenyl-(carbamoyloxymethyl-2-hydroxy-benzilidene), especially synthesised for that purpose, were also employed as quarternisation reagents [9].

A strong potential can be seen here for structural modifications of cationomers, not only by changes in types of diisocyanates and polyols used—as is the case for anionomers—but also by incorporating various dihydroxyamines in chains of tertiary urethane–isocyanate prepolymers and—as a subsequent stage—converting them in various methods to alkylammonium compounds. Therefore, utilisation of this way in the production of, for example, elastomer polyurethane coatings with additionally interesting optical performance becomes feasible. For example, a polymer material in the form of the photosensitive poly(triazene–urethane) cationomers was obtained in the poly-addition reaction of 2,4-TDI and poly(tetramethylene oxide)diol (PTMO; *M*=2,000), when *N*-MDEA and difunctional triazene compounds were used as chain extension elements. They additionally played the role of ultraviolet (UV) chromophores: 1-(*m*-hydroxymethyl)phenyl-3-(2-hydroxyethyl)-3-methyltriaz(1)ene and l-*p*-nitrophenyl-3,3-di(2-hydroxyethyl) triaz(1), and the quaternisation reaction of those phenyltriazenes involved the use of benzyl chloride. It was found under UV exposure conditions that the photolysis rate constant for so produced ionomer film was lower than that for a non-ionic polymer with the similar structure of urethane segments [10]. An original group of poly(urethaneimide) cationomers was obtained in the reaction of MDI, PTMO, *N*-MDEA and 4,4′-hexafluoroisopropylidene-bis-phthalic anhydride, when the counter-ions X^- employed were methyl sulphate, tosylate, triflate, chloride, bromide and iodide, with their alkyl groups (C_1–C_6) [11].

Not any less important are the possibilities of modifying surface properties in polyurethane cationomers and adjusting—by incorporation of cationic rigid segments—the values of surface free energy (SFE) of these materials. Those issues make the subject of the present paper.

Lower SFE values, which contribute to improved hydrophobic performance of the polyurethane surface, make a strong controlling factor for chemical affinity of that polymer for other material(s). And that, in turn, affects chemical and biological stability of that polymer in its contacts, for example, with tissues of living organisms. That issue becomes important for the use of polyurethane elastomers as biomedical materials: implants of blood vessels and temporary membranes that restore functions of internal organs that have been damaged in accidents [12, 13]. And on the contrary, by increasing the SFE value, one can improve the biodegradability of that material, which is important, for example, for safe utilisation of products after their service life [14]. It was moreover found that SFE—affecting thermodynamics of the homogenisation process—plays the essential role in the production of polymer blends with the use of polyolefines and polyurethanes [15].

The surface free energy is a physical quantity that can fairly precisely define the chemical nature of a material surface [16]. It is equal in respect of numbers to the work required to create a new unit surface when separating two phases that stay in phase equilibrium in a reversible isothermal process. The general relation between the surface free energy (γ) and the surface tension (σ) is provided by the following equation:

$$\sigma = \gamma + \mathrm{S d}\gamma / \mathrm{dS} \tag{1}$$

where *S* is the surface unit for a given body.

The notion of free surface free energy can be referred both to liquids and to solids, with the following relation applicable to liquids:

$$d\gamma / dS = 0 \Rightarrow \sigma = \gamma, \mathit{for}\, S \neq 0$$

According to the Gibbs theory, the surface tension for a solid is equal to the surface free energy only when adsorption of a liquid on a solid surface is zero.

The basis for the methods of calculating the surface free energy from the wetting angle measurement, which were used in the present work, is formulated in 1805 Young's equation:

$$\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cdot \cos \Theta \tag{2}$$

where

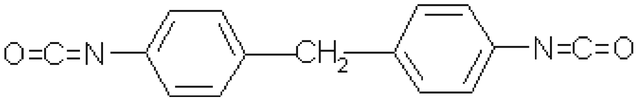
σ_{sv}	surface tension of the solid state (polyurethane coating) in equilibrium with saturated vapor of the liquid
σ_{SL}	interphase surface tension of the solid state and liquid
σ_{LV}	surface tension of the liquid in equilibrium with its saturated vapor

Having the above issues in mind, we attempted in the present study to find the correlations for structural parameters of polyurethane cationomers, which result from the employed types of raw materials and the method adopted for the synthesis process. Those parameters were the factors κ and α, which reflected polarity of cationomer structures. They were especially defined for that purpose and were found on the basis of nuclear magnetic resonance (NMR) and infrared (IR) spectra. Then, the observed trends in changes of their values were compared to the values of the surface free energy γ_{S} and its components: polar component $\gamma_{\mathrm{S}}{}^{\mathrm{LW}}$ and acid–base component $\gamma_{\mathrm{S}}{}^{\mathrm{AB}}$ in polyurethane films obtained after application of aqueous dispersions of synthesised cationomers on a non-polar surface: poly(tetrafluoroethylene).

Experimental

Raw materials and reagents

4,4′-Methylenebis(phenyl isocyanate) (MDI) from Aldrich. The reagent was used as purchased.

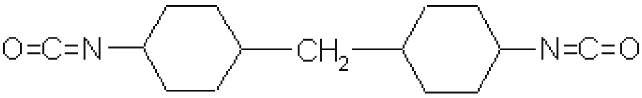


(3)

Hexamethylene-1,6-diisocyanate (HDI) from Aldrich. The reagent was used as purchased.

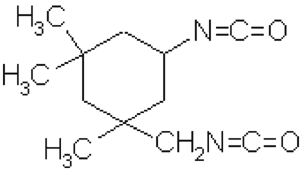
$$O = C = N(CH_2)_6N = C = O \tag{4}$$

4,4′-Methylenebis(cyclohexyl isocyanate) (HMDI) from Aldrich. The reagent was used as purchased.



(5)

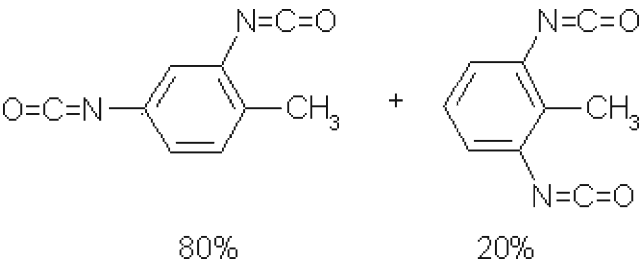
Isophorone diisocyanate [5-isocyanato-1-(isocyanato-methyl)-1,3,3-trimethylcyclo-hexane] (IPDI) from Aldrich. The reagent was used as purchased.



(6)

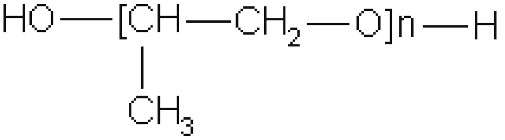
2,4-Tolylene diisocyanate (TDI) and 2,6-TDI

A technical product from Aldrich was used in the study. It was a mixture of 2,4-TDI and 2,6-TDI isomers at the ratio of 80% and 20%, respectively. The reagent was used as purchased.



(7)

Polyoxypropylene glycol (M_n=450 g/mol), Rokopol 7P from Chemical Factory “Rokita SA” in Brzeg Dolny (Poland; this product was dried under vacuum at 80 °C during 2 h).



$$HO-[CH(CH_3)-CH_2-O]n-H \tag{8}$$

N-Methyldiethanolamine (*N*-MDA; Aldrich)

$$(HO - CH_2-CH_2)_2{>}N - CH_3 \tag{9}$$

N-Phenyldiethanoloamine (*N*-PhDA; Aldrich)

$$(HO - CH_2 - CH_2)_2{>} N - C_6H_5 \tag{10}$$

1,6-Hexamethylenediamine (HMDA) from Aldrich. The reagent was used as purchased.

$$H_2N(CH_2)_6NH_2 \tag{11}$$

Dibutyl tin dilaurate (DBTL; from Huntsman Performance Chemicals)

Tetrahydrofurane (THF; from POCh SA Gliwice)

Formic acid (HCOOH), 99%, analytically pure (from POCh SA Gliwice).

Method for the synthesis of urethane cationomers

Cationomers were synthesised in the glass stand composed of a three-necked flask, heating bowl, mechanical agitator, dropping funnel, thermometer, reflux condenser and nitrogen supply nozzle. Following reactions 12–15 are the process of the obtained cationomers basic scheme. As stage 1, urethane–isocyanate prepolymer was synthesised in the reaction of selected diisocyanate (*B*) and Rokopol 7P (*A*):

$$A+2B \rightarrow AB_2 \tag{12}$$

About 10 g of diisocyanate were dissolved in 30 cm^3 of THF heated up to 50 °C. Then, Rokopol 7P was added to that solution over about 10 min. The amount of Rokopol was selected each time to maintain the relation of groups –NCO/–OH of 2:1. Also, the DBTL catalyst was added at the level of 0.1 wt%, and the reaction mixture was maintained at 50 °C over 30 min. The content of –NCO groups in the mixture was analysed after that time, and it was compared to the value calculated from the stoichiometry adopted for the process (Table 1). The findings were usually lower than expected, which makes the evidence not only for the presence of THF in the prepolymer material but predominantly for too high conversion of small amounts of initially formed trimers AB_2 with for example temporary tetramers A_2B_2 to prepolymers A_3B_4 or generally to A_{nn+1} with higher molecular weights, which was demonstrated in [17, 18].

Table 1 Chemical compositions of synthesised cationomers

Sample no.	Isocyanate prepolymer (theoretical AB_n)						Type of ionogenic reactant (Y)	Extension agent	Calculated concentration of NH^+ ions [for –$(YBAB)_n$– structure; wt%]	κ, %	α
	Substrates			n	Content of –NCO groups (wt%)						
	Type of diisocyanate (B)	Polyol (A)	Catalyst		Theoretical (for AB_n structure)	Exp.					
1	MDI	Rokopol 7P	DBTL	2.00	8.84	8.95	*N*–MDA	–	1.40	50.17	28.03
2	HDI			2.97	17.42	9.42		–	1.66	47.07	14.18
3	HMDI			1.91	16.87	5.42		–	1.37	41.05	13.75
4	IPDI			2.25	11.05	6.58		–	1.48	39.03	17.19
5	TDI			2.87	16.54	8.87		HMDA	1.63	50.28	26.60
6	MDI			2.00	8.84	7.44	*N*–PhDA	HMDA	1.33	54.23	40.75
7	HDI			2.97	17.42	9.43		–	1.55	54.34	15.97
8	HMDI			1.91	16.87	4.66		–	1.30	42.80	9.11
9	IPDI			2.25	11.05	5.43		HMDA	1.39	44.98	10.83
10	TDI			2.87	16.54	5.70		HMDA	1.53	56.97	26.83

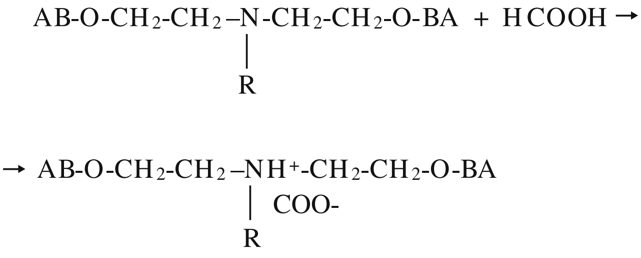
At stage 2, the prepolymer from stage 1 was reacted with *N*-methyl or *N*-phenyl diethanolamine

$$n\,AB_2 + n\,Y \rightarrow -(YBAB) - n \tag{13}$$

where Y=*N*–MDA or *N*–PhDA.

Tertiary amino groups were incorporated into the chains in that way. To do that, the selected amine was added to the flask with the prepolymer AB_2 in it at 50 °C, and the flask was maintained at that temperature over 30 min. After that time, the analysed content of –NCO groups was close to 0%.

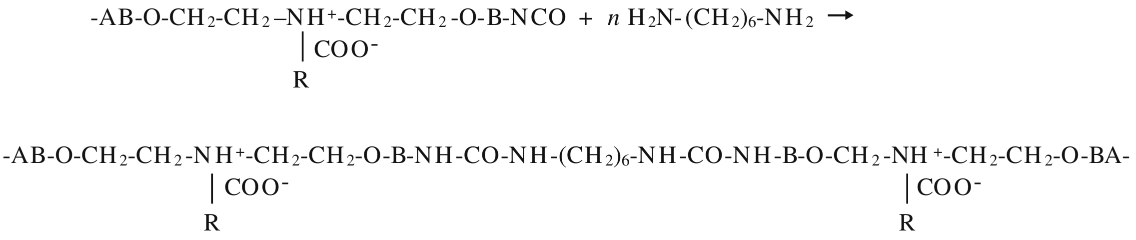
Alkylammonium cations were produced at stage 3 by protonation of tertiary amino groups with HCOOH:



$$\mathrm{AB\text{-}O\text{-}CH_2\text{-}CH_2\text{–}\underset{\underset{R}{|}}{N}\text{-}CH_2\text{-}CH_2\text{-}O\text{-}BA} + \mathrm{HCOOH} \rightarrow$$

$$\rightarrow \mathrm{AB\text{-}O\text{-}CH_2\text{-}CH_2\text{–}\underset{\underset{R}{|}}{NH^{+}}\,{}^{COO^-}\text{-}CH_2\text{-}CH_2\text{-}O\text{-}BA} \tag{14}$$

The number of moles of HCOOH to be added to the mixture was adjusted to correspond to the number of moles of built-in tertiary amine contained in the known amount of polymer. The mass fraction of NH^+ groups in so synthesised cationomers resulted from the stoichiometry assumed for the chain of reactions, and it was about 1.3–1.6 wt% (Table 1). The reaction with HCOOH was conducted at 50 ° C during 2 h and then it was allowed to continue at ambient temperature during 24 h. Redistilled water was added afterwards with a small amount of HMDA dissolved in it, under intensive agitation conditions. Water with HMDA was added during intensive prepolymers steering at 25 °C for approximately 60 min. The residual –NCO groups of the MDI and 2,4- and 2,6-TDI aromatic diisocyanates, as well as the much less reactive HDI, HMDI and IPDI diisocyanates were reacted in these conditions. The obtained homogeneous dispersion was acidic within pH=2–3, and its polymer content was about 30%. That stage was intended not only to produce the dispersion but also to extense the cationomer chains with the residual –NCO groups at the same time:



$$\mathrm{\text{-}AB\text{-}O\text{-}CH_2\text{-}CH_2\text{–}\underset{\underset{R}{|}}{NH^{+}}\,{}^{COO^-}\text{-}CH_2\text{-}CH_2\text{-}O\text{-}B\text{-}NCO} + n\,\mathrm{H_2N\text{-}(CH_2)_6\text{-}NH_2} \rightarrow$$

$$\mathrm{\text{-}AB\text{-}O\text{-}CH_2\text{-}CH_2\text{-}\underset{\underset{R}{|}}{NH^{+}}\,{}^{COO^-}\text{-}CH_2\text{-}CH_2\text{-}O\text{-}B\text{-}NH\text{-}CO\text{-}NH\text{-}(CH_2)_6\text{-}NH\text{-}CO\text{-}NH\text{-}B\text{-}O\text{-}CH_2\text{-}\underset{\underset{R}{|}}{NH^{+}}\,{}^{COO^-}\text{-}CH_2\text{-}CH_2\text{-}O\text{-}BA\text{-}} \tag{15}$$

where R=–CH_3 or –C_6H_5.

Directly after obtaining the dispersions, they were used to make polymer coatings. Continued observation showed that the water dispersions of the cationomers based on *N*–MDA are sedimentation-resistant and stabile during the storage time at least 1 month, whereas the dispersions of the cationomers based on *N*–PhDA were ply-separated during 24 h. The polymer coatings for further tests were formed by applying the above-mentioned dispersions to a non-polar surface of poly(tetrafluoroethylene) (PTFE, type Tarflen) and evaporation of water by air-drying at 20 °C. The coatings were then subjected to seasoning under such conditions over 10 days.

Determination of −NCO group content

That determination involved a well-known method, and dibutylamine was used in the tests. Excess of unreacted amine was titrated with the HCl solution, and bromophenol blue was used as an indicator [19].

NMR spectroscopy

^{1}H and carbon-13 NMR (^{13}C NMR) spectra of the obtained polymers were taken with the use of the spectrometer FT NMR Bruker Avance 500$^{\mathrm{II}}$. The samples of coatings (i.e. produced cationomers) were dissolved in DMSO–d$_6$/h–DMSO, and the solutions with the concentration of about 0.2 g/dm^3 were prepared. Tetramethylsilane was used as 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 attenuated total reflectance technique (the polymer film was placed between the prism walls. The obtained spectra were presented as the relation of transmittance (%) versus wave number $\overline{v}$ (cm^{-1}).

Method for determination of components of surface free energy for solids

Physical parameters of surface energy of a solid γ_{S} were found in the present study on the basis of the van-Oss–Good model derived from the Owens–Wendt theory. The model assumes that the surface free energy γ may be presented as a sum of two components [16, 20]:

$$\gamma = \gamma^{\mathrm{LW}} + \gamma^{\mathrm{AB}} \tag{16}$$

where

γ^{LW} surface energy connected with long-range interactions (dispersion, polar and induction interactions)

γ^{AB} surface energy connected with acid–base interactions, as results from the Lewis theory

Equation 15 is generally applicable both to a solid, marked with the subscript S, and to a wetting liquid (standard liquid or tested liquid), marked with the subscript L.

Let us use the symbol γ_S^+ for the component of γ_S^{AB}, which is responsible for the surface free energy of the Lewis acid, and the symbol γ_S^- for the component representing the Lewis base. On the basis of the Berthelot theory, which assumes that interactions between molecules of different bodies located on a surface are equal to the geometric mean of interactions between molecules within each of those bodies, one can now formulate the following relations [16, 21]:

- For bipolar substances (liquids and surfaces of solids), which can be equivalent to synthesised PU ionomers, present in the form of aqueous dispersions or coatings:

$$\gamma_i^{\mathrm{AB}} = 2\left(\gamma_i^+ \gamma_i^-\right)^{0.5} \tag{17}$$

- For non-polar liquids and surfaces of solids (diiodomethane and PTFE):

$$\gamma_i^{\mathrm{AB}} = 0 \tag{18}$$

(where *i*=*S*—solid, *L*—liquid).

The surface free energy parameters for solids (*S*) and for liquids (*L*) interacting with those solids should satisfy the equation of van-Oss–Good:

$$\left(\gamma_S^{\mathrm{LW}} \gamma_L^{\mathrm{LW}}\right)^{0.5} + \left(\gamma_S^+ \gamma_L^-\right)^{0.5} + \left(\gamma_S^- \gamma_L^+\right)^{0.5} = \gamma_L(1+\cos\Theta)/2 \tag{19}$$

where Θ is the experimentally found wetting angle between a liquid drop and a solid surface under investigation. Therefore, wetting angles Θ were first measured for the surfaces of cationomer coatings with the use of three model liquids (water, diiodomethane and formamide) with known parameters γ_{L}, $\gamma_{\mathrm{L}}^{\mathrm{LW}}$, γ_{L}^+ and γ_{L}^- (Table 5), and then the Eq. 18 was used to calculate the values $\gamma_{\mathrm{S}}^{\mathrm{LW}}$, γ_{S}^+ and γ_{S}^- for the studied cationomers. The values $\gamma_{\mathrm{S}}^{\mathrm{AB}}$ were calculated from Eq. 17, while the values γ_{S} were calculated from Eq. 16.

The angles Θ were measured with the use of the method suggested by Zisman [22], i.e. by means of optical goniometer (Cobrabid Optica—Warsaw) with a digital camera installed instead in axial extension of its lens. The liquid drops with the constant volume (about 3–5 μdm^3) were applied to the surfaces of studied samples with the use of a special micropipette. The samples were fixed on the stage of the goniometer. The measurements were taken in a room at 21±1 °C. The values of wetting angles were found from the geometric analysis of pictures taken for liquid drops, which involved the use of the original software developed by Kontrast (Pasłęk, Poland) for interpretation of the Young's equation. The measuring errors for angles Θ come from two sources. The first of them results from different shapes of liquid drops placed on the investigated coatings and from possible interactions between the standard liquid and that subgrade, as well as from different liquid vaporisation rates observed when the pictures were taken. Nine drops were analysed each time, which were placed on the surface simultaneously. Another source of potential errors is inaccuracy in graphical interpretation of the pictures with the use of the computer software. For each picture recorded (i.e. for each liquid drop), the geometrical shape analysis was repeated ten times: The extreme values were rejected, and the arithmetic mean value was calculated for the accepted findings. All of the accepted angle Θ_i values for each of the synthesised sample (1–10), referring to the determined model measuring fluid, were used to the wetting angle average value and standard deviation calculation. The measured values of wetting angles, standard deviations and the components of the surface free energy for the cationomer coatings as derived from those measurements were presented in Table 6. Analysing the obtained results, it is essential to remember that the method of determining wetting angles that was used here, despite of all the carefulness during measurements, is characterised by not too high reproducibility, what proves, for example, quite high values of the wetting angle standard deviations as it is for sample 10 (Table 6), what influences in consequence on the accuracy of the obtained surface free energy component values.

Results and discussion

Chemical structures and polarity nature of cationomers

The chemical structures of the synthesised cationomers were precisely established on the basis of H^1 and C^{13} NMR spectra. Figure 1 shows the formulas for structural fragments that make up the polymer chains of those cationomers. The exemplary H^1 and C^{13} NMR spectra for cationomer 1 synthesised from the aromatic diisocyanate MDI and *N*–MDA are presented in our earlier article [23]. Figures 2 and 3 make illustrations of spectra for cationomer 3 synthesised from the cycloaliphatic diisocyanate HMDI. The detailed interpretations for those spectra can be found in Table 2.

The presented spectra explicitly confirm the structures of synthesised cationomers. Single signals representing aromatic protons (*k*) and (*l*) observed for cationomers 3 and 4, which have been produced from cycloaliphatic diisocyanates HMDI or IPDI, respectively, and from *N*–MDA, result from the small amounts of aromatic impurities present in the purchased reagents. The signals recorded in C^{13} NMR spectra of those polymers in the locations typical for aromatic ring carbon atoms δ=115–140 ppm do not stand out in practice from the recorded noise. The most important signals, which confirm the structures of the obtained polyurethanes, represent urethane protons (*x*) and urea protons (*q*), which are not present in the substrates, as well as from $–CH_2–$ groups (*e*) bounded directly to urethane groups or urea groups. These are C atoms in C^{13} NMR spectra that have been designated 5 and 8 in Fig. 1. On the other hand, the signals for protons (b) and (z), and for carbon atoms (7) and (14) make the evidence for the presence of ionic structures in the studied cationomers.

Based on integrated signals of H^1 NMR spectra, polarity of chemical structures of synthesised cationomers was evaluated. The factor as follows was defined for that purpose:

$$\kappa = \frac{I_p}{I_p + I_N} \cdot 100\% \tag{20}$$

where

$$I_p = \sum \left(I_b + I_f + I_t + I_u + I_e + I_y + I_m + I_z + I_x + I_q \right) \tag{21}$$

is the sum of integrated signals recorded over a wide span of δ=3.0–5.0 ppm (designated as *b*, *f*, *t*, *u*, *e*, and *m*) and representing the protons in groups CH_2 and CH bonded to polar ether groups, to nitrogen atoms, to groups –OH, to urethane groups or urea groups, (sum of) signals for protons of free –OH groups (*y*) and polar groups NH in urethanes, urea compounds and allophanates (*x*, *q*), as well as protons (*z*) in NH^+ group, which has been neutralised with the formate anion COO^-, while

$$\mathrm{I_N} = \sum \left(I_a + I_r + I_s + I_n + I_p + I_w + I_c + I_d + I_g + I_h + I_{\mathrm{arom}} \right) \tag{22}$$

is the sum of integrated signals for protons of non-polar groups $–CH_3–CH_2$ and –CH–, which are present in structural units derived from Rokopol 7p (*a*), from the employed diisocyanate and HMDA amine chain extender HMDA (*r*, *s*, *m*, *p*, *w*, *d*, *g*, and *h*), from dihydroxyethanoloamine (*c*) and signals for protons of aromatic structures derived from PhDEA (cationomers 6–10) and urethane derivatives of MDI and TDI. The signals of potential aromatic impurities present in cycloaliphatic diisocyanates HMDI and IPDI have also been considered.

With that assumption, Eq. 20 gives the shares of chemical structures that have the dominant effects on polar interactions, while Eq. 20 is specific for non-polar interactions that take place in the structures of synthesised cationomers (Fig. 1; Table 3). One can assume than that the value for the factor κ, as calculated from Eq. 19, provides

$\ldots\text{—}R_{1\text{-}5}\text{—}A\text{—}R_{1\text{-}5}\text{—}Y_{1\text{-}2}\text{—}R_{1\text{-}5}\text{—}Z\text{—}R_{1\text{-}5}\text{—}A\text{—}R_{1\text{-}5}\text{—}Y_{1\text{-}2}\text{—}R_{1\text{-}5}\text{—}A\text{—}\ldots$

where:

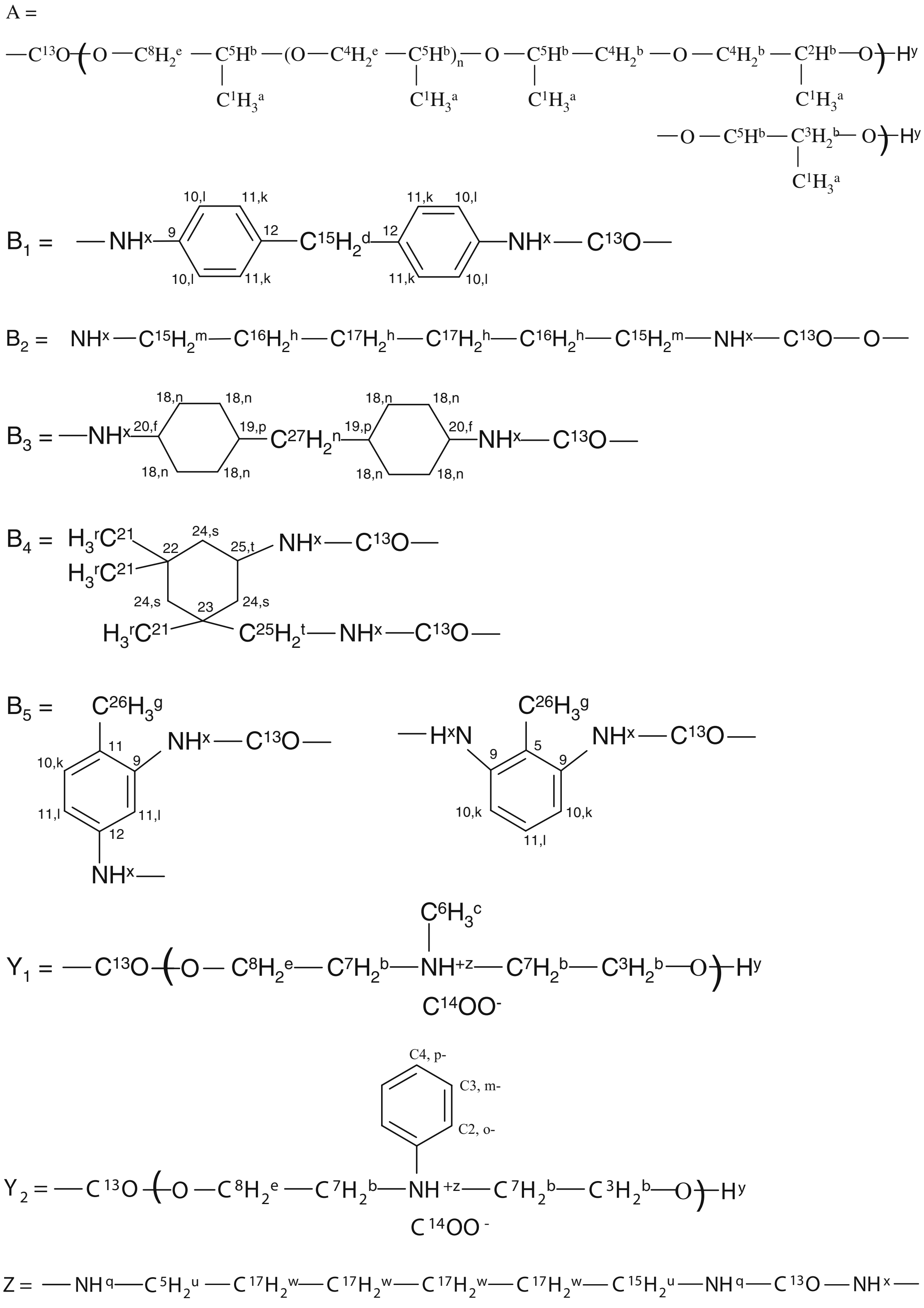


Fig. 1 Chemical structures of polyurethane cationomers

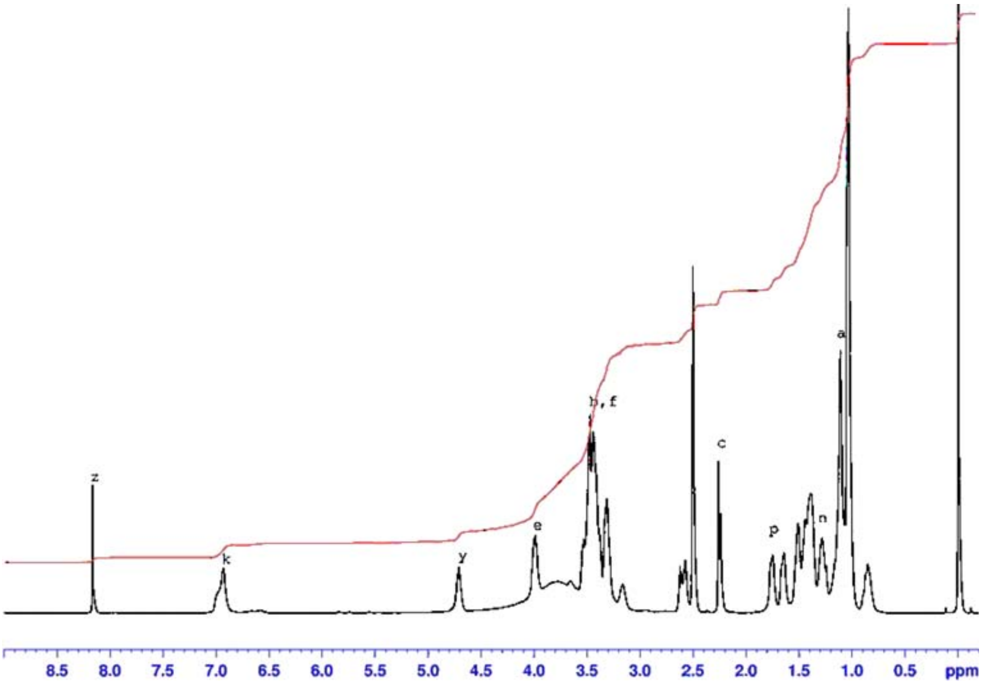


Fig. 2 H^1 NMR spectrum of cationomer 3 synthesised with cycloaliphatic diisocyanate HMDI and *N*–MDA

physical characterisation of the polarity degree for a given cationomer. The obtained data show that the values calculated for the factor κ vary within 39–50% for the group of cationomers synthesised with the use of *N*–MDEA and within 43–57% for the group of cationomers synthesised with the use of *N*–PhDA. The highest values of κ in both those groups was observed for cationomers 5 and 1, and 10 and 6, synthesised from TDI and MDI diisocyanates, as well as for cationomer 7, synthesised from HDI and aromatic amine *N*–PhDA. The ratio α calculated on the basis of IR spectra:

$$\alpha = \frac{A_p}{A_{2870-2931}} \tag{23}$$

was adopted as the additional criterion for evaluation of polarity of chemical structures of synthesised cationomers.In Eq. 23,

$$A_p = A_{3100-3400} + A_{1700-1730} + A_{1520-1540} + A_{1180-1280} \tag{24}$$

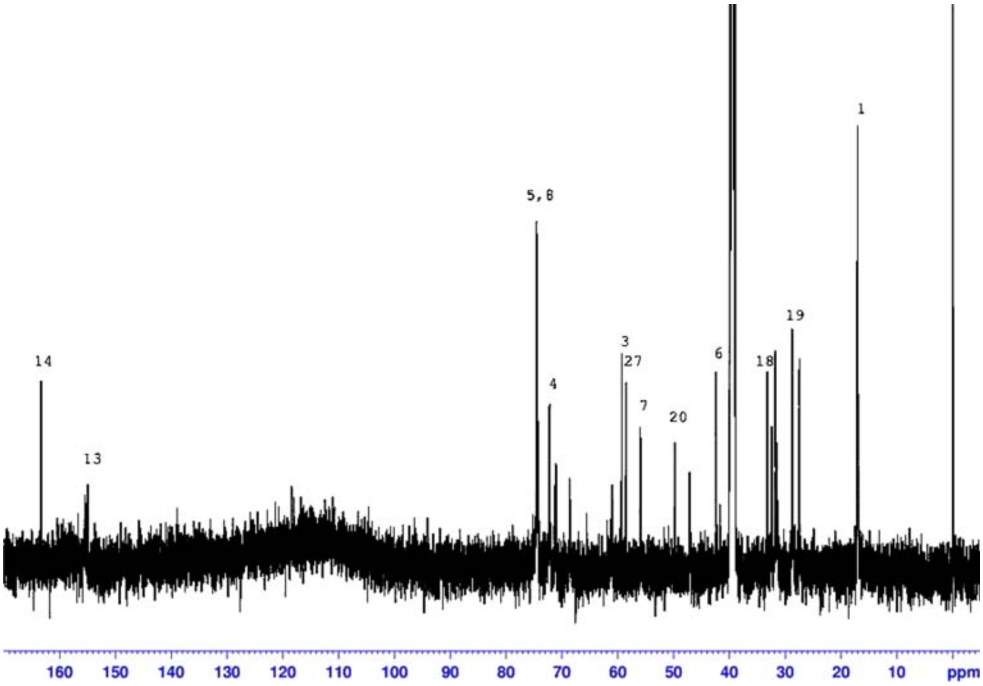


Fig. 3 C^{13} NMR spectrum of cationomer 3 synthesised with cycloaliphatic diisocyanate HMDI and *N*–MDA

Table 2 Interpretation of polyurethane cationomer NMR spectra

Type of nucleus (Fig. 1)	Sample no.									
	1	2	3	4	5	6	7	8	9	10
	Chemical shift *δ*, ppm									
H^1 NMR spectra										
a	1.00–1.33	1.04–1.36	0.80–1.39	0.80–1.13	1.03–1.19	1.02–1.19	1.10–1.22	0.86–1.12	0.80–1.12	1.03–1.19
r	–	–	–		–	–	–			–
n	–	–	1.44–1.51	–	–	–	–	1.28–1.51	–	–
s	–	–	–	1.24	–	–		–	1.44	–
h	–	1.36	–	–	–	–	1.36	–	–	–
w	–	–	–	–	1.75–1.77	1.75–1.77	–	–	1.74–1.77	1.75–1.77
p	–	–	1.64–1.75	–	–	–	–	1.66–1.77	–	
g	–	–	–	–	2.12–2.18	–	–	–	–	2.13–2.18
c	2.29	2.23	2.24	2.25	2.30	–	–	–	–	–
DMSO	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
H_2O in DMSO	2.67	2.72	2.62	2.72	2.70	–	–	–	2.73	–
m	–	2.94	–	–	–	–	2.95	–	–	
b	3.22–3.77	3.32–3.55	b and f	b and t	b and u	b and u	b and u	b and f	b and t and u	b and u
f	–	–	3.16–3.54	–	–	–	–	3.17–3.62	–	–
t	–	–	–	3.38–3.66	–	–	–	–		–
u	–	–	–	–	3.32–3.62	3.32–3.77	3.32–3.64	–	3.32–3.62	3.32–3.64
d	3.80	–	–	–	–	3.80	–	–	–	–
e	4.14	3.99	4.00	4.00	4.13	4.20	4.05	4.05	4.06	4.20
y	4.86	4.72	4.72	4.72	4.85	4.86	4.72	4.72	4.72	4.85
k	7.06	$7.0_{\text{arom.}}$ impurity	$6.93_{\text{arom.}}$ impurity	$7.0_{\text{arom.}}$ impurity	7.06	7.1	–	–	–	7.07–7.17
l	7.35	–	–	–	7.35	7.34–7.35	–	–	–	7.50
o–	–	–	–	–	–	6.6	6.6	6.6	6.6	6.6
m–	–	–	–	–	–	6.8	6.8–7.2	6.8	6.7–7.1	6.8–7.1
p–	–	–	–	–	–	7.1		7.1		
Z	8.15	7.98	8.17	8.15	8.15	8.50	–		–	7.92
q	–	–	–	–	8.77	q and x				8.82
x	9.51	8.40	–	–	9.50	9.49–9.54				9.52
C^{13} NMR spectra										
26	–	–	–	–	12.92	–				12.0
1	16.8–17.1	17.0–17.2	17.0–17.2	17.0–17.2	16.8–17.2	16.8–17.2	17.0–17.2	17.0–17.2	17.0–17.2	16.8–17.3
21*eq*	–	–	–	23.07	–	–	–	–	23.07	–
22	–	–	–	27.41	–	–	–	–	27.39	–
16	–	28.8–29.9	–	–	–	–	29.28	–	–	–
17	–	25.5–26.0	–	–	25.03	25.03	25.86	–	–	25.03
18, 19	–	–	31.45, 31.77	–	–	–	–	31.49, 31.78	–	–
21*ax*	–	–	–	31.20	–	–	–	–	31.20	–
15	≈40	–	–	–	–	≈40	–	–	–	–
23	–	–	–	34.9	–	–				
DMSO	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	40.5	
6	42.19	42.32	42.30	41.29	42.2	–	–	–	–	–
24	–	–	–	43.69		–			43.70	
25	–	–	–	46.53	–	–	–	–	46.54	
27	–	–	58.53	–	–	–	–	58.0	–	–
7	55.68	55.86	55.83, 56.95	54.21	55.75	49.26	49.39	53.15	53.14	49.24
20	–	–	47.73	–	–	–	–	47.73	–	
3	61.73	61.37	61.02	61.46	61.95	60.99	60.47	60.36	60.61	–
2	65.24	–	–	–	66.93	66.92	–	66.93	66.93	66.93

Table 2 (continued)

Type of nucleus (Fig. 1)	Sample no. 1 Chemical shift δ, ppm	2	3	4	5	6	7	8	9	10
4	72.26, 72.06	72.33.72.10	72.34, 72.12	72.32, 72.10	72.27, 72.06	72.25, 72.07	72.31, 72.10	72.32, 72.13	72.33, 72.09	72.27, 72.09
5, 8	74.2–74.6	74.2–74.6	74.2–74.6	74.1–74.5	74.1–74.6	74.5	74.2–74.7	74.2–74.6	74.1–74.5	74.4–74.6
10	118.20	–	–	–	115.00	118.21	–	–	–	115.87
11	128.70	–	–	–	130.02	128.71, 129.15	–	–	–	130.04
*C*1	–	–	–	–	–		129.06	129.00, 128.91	129.00, 128.91	
9	136.97	–	–	–	137.0–	135.49,	–	–	–	136.15,
12	137.07	–	–	–	138.0	137.09	–	–	–	137.20
*C*2	–	–	–	–	–		115.72	115.26, 114.88	115.28, 114.88	
*C*4	–	–	–	–	–	147.09	147.24	147.57, 147.81	147.56	
13	153.03, 253.40	155.74, 156.07	155.42, 154.92	156.70, 154.94	154.17, 153.02	153.42, 154.92	156.05, 155.73	155.43, 154.92	157.76, 154.94	154.18, 153.00
14	163.06	165.33	163.28	163.06	163.09					

is the sum of absorbance values measured for maxima of polar group bands recorded within the following ranges: 3,100–3,400 cm^{-1} representing valence vibrations of N–H in urethanes and urea compounds ($A_{3100–3400}$), 1,160–1,730 cm^{-1} representing valence vibrations of C=O in urethanes and urea compounds ($A_{1630–1730}$), 1,520–1,540 cm^{-1} representing deformation vibrations of N–H in urethane group ($A_{1520–1540}$) and 1,180–1,280 cm^{-1} representing valence vibrations of C–O in ethers and alcohols ($A_{1180–1280}$), while $A(_{2870–2931})$ is the absorbance of a single band within 2,870–2,931 cm^{-1},

Table 3 Analysis of signal integration in NMR spectra of synthesised cationomers

Sample no.	1	2	3	4	5	6	7	8	9	10
Integration (conventional unit)										
I_b	4.84	27.18	–	–	–	–	–	–	–	–
I_b+I_f	–	–	32.87	–	–	–		12.85	–	–
I_b+I_t	–	–	–	22.32	–	–		–	10.44	–
I_b+I_u	–	–	–	–	14.02	13.62	7.24	–	–	20.60
I_e	0.50	7.47	5.13	4.42	2.13	1.12	1.04	0.77	0.87	1.73
I_y	0.18	3.34	1.98	1.91	0.93	0.48	0.29	1.13	0.73	1.00
I_m	–	10.85	–	–	–	–	1.64	–	–	–
I_z	0.11	1.46	0.93	1.06	0.88	0.10	0	0	0	0.73
I_x+I_q	0.49	1.00	0	0.62	2.46	1.03	0	0	0	2.60
I_{P}	6.12	51.30	40.91	30.33	20.42	16.35	10.21	14.75	12.04	26.66
I_a	3.00	40.66	30.50	–	9.79	6.12	4.70	6.05	–	9.55
I_a+I_r	–	–	–	37.61	–	–	–	–	8.99	–
I_s	–	–	—	4.36	–	–	–	–	2.40	–
I_n+I_p	–	–	22.60	–	–	–	–	10.05	–	–
I_w	–	–	–	–	0.46	0.64	–	–	0.58	1.51
I_c	0.30	3.21	2.94	2.49	1.79	–	–	–	–	–
I_d	0.60	–	–	–	–	1.12	–	–	–	–
I_g	–	–	–	–	5.01	–	–	–	–	3.58
I_h	–	13.82	–	–	–	–	1.68	–	–	–
I_{arom}	2.08	–	2.72	2.92	3.14	5.92	2.20	3.61	2.76	5.50
I_{N}	5.98	57.69	58.76	47.38	20.19	13.80	8.58	19.71	14.73	20.14
κ	50.58	47.07	41.05	39.03	50.28	54.23	54.34	42.80	44.98	56.97

Table 4 Analysis of absorbance values of selected IR spectra for synthesised cationomers

Sample no.	1	2	3	4	5	6	7	8	9	10
$A_{3100–3400}$ (conventional scale)	0.3403	0.2254	0.2795	0.1902	0.3807	0.3280	0.2006	0.2464	0.2664	3.4751
$A_{1630–1730}$ (conventional scale)	2.4028	3.1053	3.0270	2.5519	1.5914	1.1274	2.1262	0.9422	0.9160	10.317
$A_{1520–1540}$ (conventional scale)	1.8211	1.6300	1.5672	1.3696	0.8203	2.2724	0.7157	0.8431	0.8410.	4.7407
$A_{1280–1180}$ (conventional scale)	2.1031	1.0954	2.1302	1.3913	2.3145	1.2763	2.4088	2.4349	1.4823	0.5825
A_{P}	6.6673	6.0561	7.0079	5.5030	5.1069	5.0041	5.4513	4.4666	3.5057	15.6402
$A_{2870–2931}$ (conventional scale)	A_{2927}=0.2379	A_{2931}=0.4271	A_{2924}=0.5095	A_{2924}=0.3201	A_{2925}=0.1920	A_{2870}=0.1228	A_{2929}=0.3414	A_{2925}=0.4901	A_{2925}=0.3237	A_{2973}=0.5830
α	28.03	14.18	13.75	17.19	26.60	40.75	15.97	9.11	10.83	26.83

with the highest intensity, representing valency vibrations of C–H in alkyl groups. The results of calculations were presented in Table 4.

Essentially, all the considered analytical bands in the analysed IR spectra offer generally high intensities; i.e. one can assume that their molar extinction coefficients ε have nearly the same values; hence, they can be neglected when building up Eq. 20, which characterises only the relative shares of functional groups. For example, Fig. 4 shows IR spectra of cationomer 1 synthesised from the aromatic diisocyanate MDI, with the use of *N*–MDA.

Unlike parameter κ, the higher the value of parameter α is, the higher role can be attributed to polar interactions in macromolecules of investigated cationomers.

Surface free energy parameters

Table 6 provides the values of wetting angles Θ as found, as well as components of surface free energy calculated on the basis of those angles in accordance with the procedure as mentioned above for coatings obtained from the studied polyurethane cationomers. The wetting angle between each coating and the measuring liquid was found after application of nine drops of the liquid on the surface of that coating. The wetting angle value for each drop is the average of ten calculations from the computer interpretation of the Young's equation. Hence, the findings presented in Table 6 make formally the average of 90 values of Θ_{i} obtained for each coating wetted with the given standard liquid. All the obtained results were then considered when the specified values of standard deviation were calculated. The highest errors are noticeable for the values of Θ_{i} obtained for cationomer 10, which affects the errors of the calculated values of surface free energy components.

The obtained polyurethane coatings are characterised by the surface free energy $\gamma_{\mathrm{S}}>32$ mJ/m^2, which justifies their classification as medium polar materials. For comparison, the values of γ_{S} for apolar polymers are much lower; e.g. Tarflen used in this study as a subgrade for coatings has the energy $\gamma_{\mathrm{S}}=21.8$ mJ/m^2 [24]. The highest values of γ_{S} were found for polyurethane cationomers obtained from aromatic diisocyanates MDI and TDI (samples 1, 5, 6 and 10), i.e. $\gamma_{\mathrm{S}}\approx40$ mJ/m^2 in both series of cationomers synthesised with the use of *N*–MDA and *N*–PhDA. The lowest value of $\gamma_{\mathrm{L}}^{\mathrm{LW}} = 33\,mJ\big/m^2$ was noted for the cationomer coating 8—that was synthesised from HMDI and *N*–PhDA. Hence, it is the diisocyanate-derived structure of the urethane segment to be decisive for the surface free energy.

Figure 5 illustrates the effects of chemical structures present in cationomers synthesised from various diisocyanates on polarity of those cationomers, as described with the use of factors κ and α, and on the values of surface free energy γ_{S} of polyurethane coatings obtained from those

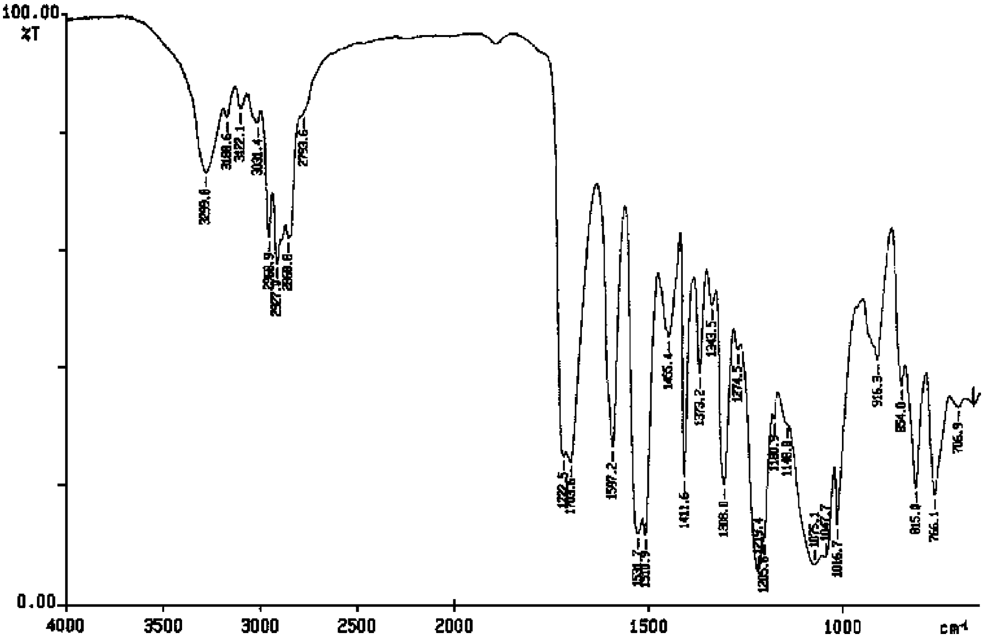


Fig. 4 IR spectrum of cationomer 1 synthesised with aromatic diisocyanate MDI and *N*–MDA

cationomers. Those effects have been presented separately for the series of cationomers synthesised with the use aliphatic amine (*N*–MDA) and aromatic amine (*N*–PhDA) as a compound responsible for ionic interactions. The presented diagrams suggest that the correlation between the parameters κ and α, and the values of γ_S yields first of all from the fact that—in case of all analysed cationomers—the basic contribution to γ_S comes from the component connected with the dispersion interactions $\gamma_\mathrm{S}^\mathrm{LW}$. And these result predominantly from the presence of polar structural fragments of cationomers. The quantitative shares of those fragments were established with the use of NMR and IR methods.

It should be emphasised that, when the correlation between the values of parameters κ and α and the values of γ_S is mentioned above, one should have in mind only the fact that the increase in structural factors κ and α corresponds to the observable increase in parameters γ_S and $\gamma_\mathrm{S}^\mathrm{LW}$. That is well illustrated by diagrams shown in Fig. 5. There is no justification, however, for comparing the numerical values of those quantities because these have been expressed in units that do not correspond to each other. As results from Eq. 20, parameter κ is given in percent, parameter α—as defined by Eq. 23—is a dimensionless quantity, while γ_S and its components are specified in millijoules per square meter.

After analysing the obtained data, one can arrive at the conclusion that the extent of dispersion interactions (most essential in cationomers) is decided principally by the structure of PU macromolecules, i.e. by the chains composed of flexible polyol segments, derived from Rokopol 7P, and of rigid—i.e. more polar—urethane segments that involve, for example, diisocyanates and tertiary amines, and possibly urea-derived segments formed in the reaction of diisocyanates with the amine chain extended (HMDA). On the other hand, no clear contribution was observed from the component $\gamma_\mathrm{S}^\mathrm{AB}$ to the total surface free energy γ_S. That probably results from low and nearly the same amounts (i.e. within 1.3–1.5%) of NH^+ cations (Table 1) incorporated to cationomer chains. Although cationic groups have been neutralised with COO^- counter-ions at the stage of synthesis, this should not lower the value of $\gamma_\mathrm{S}^\mathrm{AB}$ for ionomers capable of dissociating in water. Definitely higher parameters are characteristic for the Lewis base component γ_S^-, which results from the counter-ion COO^-; the presence of that counter-ion has been observed in C^{13} NMR spectra (signal 14). However, the adopted calculation procedure, which is based on the van Oss–Good method, does not make it possible to compare directly the components of surface free energy that result from acid- and base-type interactions in the same polymer because those values come from the arbitrary ratio of $\gamma_\mathrm{S}^+/\gamma_\mathrm{S}^-$, which has been assumed for water (as a measuring liquid) to be equal to 1 (Table 5) [19].

Table 5 Surface properties of the model measuring fluids [20]

Model measuring fluids	Surface free energy parameters (mJ/m²)				
	γ_L	$\gamma_\mathrm{L}^\mathrm{LW}$	$\gamma_\mathrm{L}^\mathrm{AB}$	γ_L^-	γ_L^+
Water	72.8	21.8	51	25.5	1.6
Formamide	58.0	39.0	19.0	39.6	0.9
Diiodomethane	50.8	50.8	0	0	0

Table 6 Comparison of the results for contact angles determinations and calculated values of surface free energy components of synthesised polymer cationomers

Sample no.	Average contact angle Θ (°; standard deviation)			Surface free energy components (mJ/m^2)				
	Model measuring fluids							
	Water	Formamide	Diiodo-methane	γ_S	γ_L^{LW}	γ_L^{AB}	γ_L^+	γ_L^-
1	64.2 (1.2)	48.9 (1.3)	31.2 (1.5)	42.62	38.21	4.41	0.32	4.41
2	52.1 (1.6)	49.3 (1.4)	40.1 (1.2)	39.43	34.59	4.84	0.19	31.50
2	78.4 (1.4)	58.7 (1.3)	38.5 (1.1)	37.81	35.26	6.10	0.27	6.10
4	78.8 (1.4)	54.6 (1.3)	47.2 (1.1)	36.20	31.30	4.90	1.59	3.78
5	67.0 (0.8)	44.4 (0.9)	37.2 (1.0)	43.49	35.83	7.66	1.46	9.87
6	68.7 (1.6)	52.5 (1.4)	31.5 (1.7)	41.22	38.10	3.22	0.20	12.33
7	80.1 (1.1)	65.10 (1.1)	42.2 (1.0)	39.28	33.53	5.74	0.01	8.23
8	82.6 (1.2)	62.0 (1.3)	52.9 (0.9)	32.76	28.52	4.25	1.07	4.23
9	72.9 (1.0)	60.9 (1.1)	50.8 (1.1)	33.85	29.58	4.27	0.36	12.67
10	70.9 (2.9)	51.6 (6.2)	36.1 (4.3)	40.95	36.31	4.64	0.55	9.77

Comparison is possible, on the other hand, within the values of γ_S^+ or γ_S^- if they refer to different cationomers. Within the cationomers studied, the highest value of the acid-type component $\gamma_S^+ = 1.5\,mJ/m^2$ is specific for cationomers 4 and 5 obtained with the use of the aliphatic amine *N*–MDA, while much lower value of $\gamma_S^+ = 0.01\,mJ/m^2$ is specific for cationomer 7 obtained from the aromatic amine *N*–PhDA. The values of γ_S^+ for other cationomers are

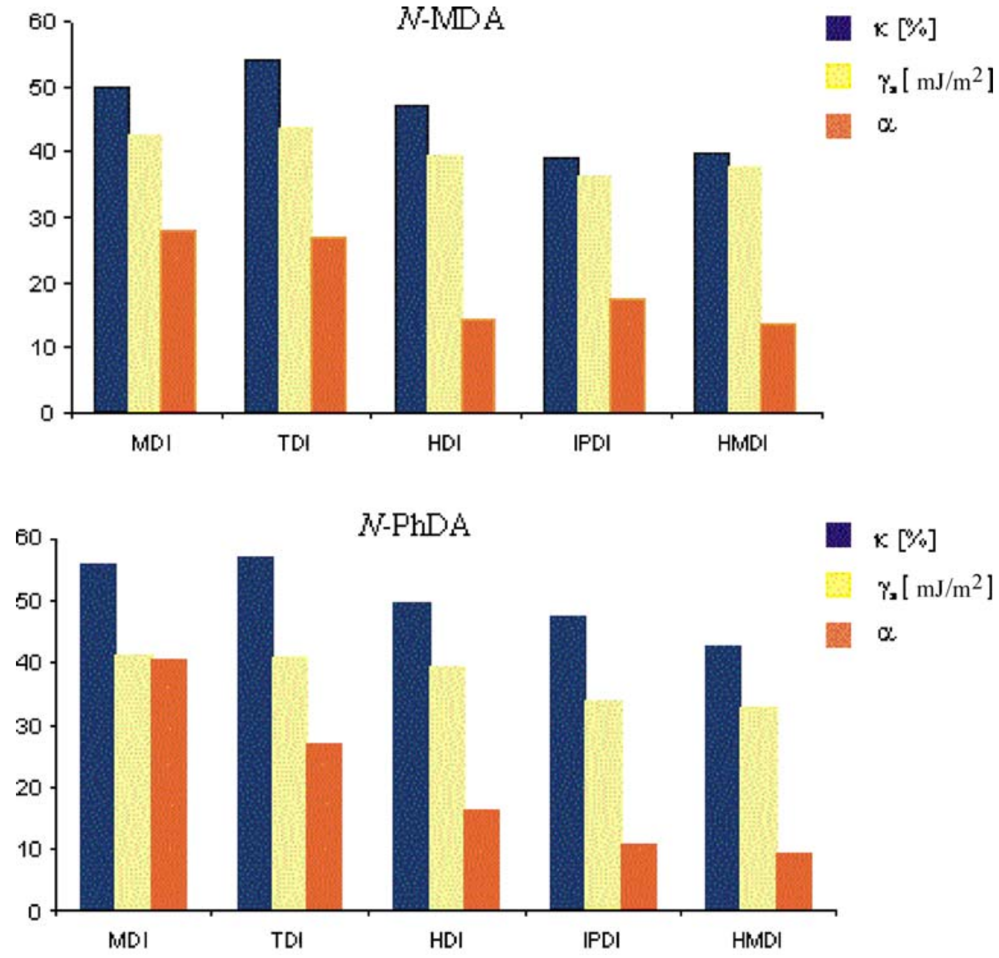


Fig. 5 Graphical illustration of effects from chemical structures of cationomers synthesised from various diisocyanates on polar specifications of those cationomers expressed by coefficients κ and α, and on surface free energy values γ_S of polyurethane coatings obtained from those cationomers

similar, and they fall within the range of 0.2–0.6 mJ/m^2. Much higher and much more diversified values were noted for the component γ_S^-. The highest values of $\gamma_S^- = 31.5$ and 12.5 mJ/m^2 were observed for cationomers 2 and 6, respectively, and the lowest values of $\gamma_S^- = 4.2$ for cationomers 1 and 8. No clear explanation can be provided for those differences at the present stage of this study. They most probably result from different locations of ionic structures in the chains of synthesised cationomers. That problem is planned to make the subject of our further research stage, wherein the effects of amount(s), structure (s) and location(s) of the cation segment within the chain of linear polyurethane will be analysed.

What should be noted is that, as we have found out in our earlier studies on polyurethane anionomers, the value of surface free energy γ_S and its components can be decided not only by the polarity and ionic nature of the polymer (these result from the chemical structures of macro-molecules, and their effects can be evaluated on the basis of factors α and κ) but probably also as observed for anionomers by the sizes of created macro-molecules, by distribution of their molecular weights and even by the type of organisation of supermolecular structures [1, 2].

Conclusions

Our investigations have shown that the use at respective stages of the poly-addition process of various diisocyanates and tertiary amines that can be incorporated to urethane prepolymer chains and that (amines) would react with carboxylic acids to yield stable cationic sites makes it possible to produce water-soluble polyurethane cationomers. These, after application to a PTFE subgrade and evaporation of solvents, give coatings with diversified values of surface free energy. The NMR and IR spectral methods confirm the expected structures of those cationomers. Based on the analysis of integrated signals in H^1 NMR spectra, one can calculate the parameter κ, which represents the degree of polarity of synthesised cationomers. The analogical parameter α can be found from the analysis of absorbance values of selected bands in the IR spectrum.

The obtained findings subjected to analysis justify the statement that it is possible to establish the correlation—qualitative only at the present stage of our research—between the structural parameters κ and α of polyurethane cationomers, which define the polar nature of cationomers, and the values of their surface free energy γ_S and its dispersion component γ_S^{LW}, as found from the measured values of wetting angles on the basis of the van-Oss–Good model.

It is advisable to expand the research to establish a more precise correlation between the structure of the cationomer chain and the Lewis-type component γ_S^{AB} of surface free energy γ_S and its acid–base components γ_S^+ and γ_S^-, as found from the adopted van-Oss–Good model. The acid–base interactions in cationomers should bring the essential contribution to the formation of stable aqueous dispersions of polyurethane cationomers, which—as can be found in references—are applicable *inter alia* as environmentally friendly lacquers and binders. The issues discussed in the present study are essential also because the surface free energy of the polymer is decisive for its chemical and biological stability and for its susceptibility to surface modifications, e.g. during colouration and surface over-prints, and it affects adhesion of lacquer coatings to metal surfaces to be protected. Those properties are important, e.g. for applications of polyurethane cationomers, as selective polymeric membranes, anticorrosion finishes obtained from aqueous dispersions, binders and adhesives, and for applications of polyurethane items as modern medical implants.

References

1. Król P, Król B, Holler P, Telitsyna N (2006) Colloid Polym Sci 284:1107
2. Król P, Król B, Holler P, Pikus S, Kozak M (2006) Colloid Polym Sci 285:169
3. Król P, Król B, Subocz L, Andruszkiewicz P (2006) Colloid Polym Sci 285:177
4. Król P, Król B (2004) Polimery 49:615
5. Król P, Król B (2007) Polimery 52:427
6. Meng-Shung Y, Hsiang-Chin T, Po-Da H (2006) J Appl Polym Sci 100:2963
7. Siwoń U, Drobionka J (1999) Pol. Patent no. 335466
8. Sudipta M, Krishnamurti N (1997) J Appl Polym Sci 62:1993
9. Buriana EC, Olaru M, Olaru M, Strat M, Strat G, Simionescu BC (2005) Polym Int 54:1296
10. Buriana EC, Niculescu V, Buriana T (2003) J Appl Polym Sci 88:1203
11. Awkal M, Jonquieres A, Lochon CR (2006) Polymer 47:5724
12. Poussard L, Burel F, Couvercelle JP, Merhi Y, Tabrizian M, Bunel C (2004) Biomaterials 25:3473
13. Gorna K, Gogolewski S (2003) Polym Degrad Stab 79:465
14. van Minnen B, Stegenga B, van Leeuwen BM, van Kooten TG, Bos RRM (2006) J Biomed Mater Res A 76A:377
15. Pötschke P, Walheinke K, Fritsche H, Stutz H (2004) J Appl Polym Sci 64:749
16. Good JR (1991) Fundamentals of adhesion. In: Lee LH (ed) Dekker, New York, p 153
17. Król P, Pilch-Pitera B (2003) Eur Polym J 39:1229
18. Król P, Pilch-Pitera B (2003) Polymer 44:5075
19. Stagg HE (1966) Analyst 71:557
20. Żenkiewicz M (2006) Polimery 51:169 (also 51:584)
21. van Oss CJ (1988) Chem Rev 88:927
22. Zisman WA (1964) Adv Chem (Am Chem Soc) 43:1
23. Król P, Król B (2008) Colloid Polym Sci in press. doi:10.1007/s00396-008-1870-6
24. Król P, Król B (2006) J Eur Ceram Soc 26:2241