Colloid Polym Sci (2008) 286:1111–1122
DOI 10.1007/s00396-008-1870-6

ORIGINAL CONTRIBUTION

Polyurethane cationomers synthesised with 4,4′-methylenebis (phenyl isocyanate), polyoxyethylene glycol and *N*-methyl diethanolamine

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Received: 8 October 2007 / Revised: 8 January 2008 / Accepted: 17 March 2008 / Published online: 24 April 2008

Abstract Polyurethane cationomers with increased contents of ions were synthesised in the reaction of 4,4′-methylenebis (phenyl isocyanate) (MDI) with polyoxypropylene glycol (M=450) and *N*-methyl diethanolamine (*N*-MDA). Amine segments were built-in to the urethane–isocyanate prepolymer in the reaction with formic acid and then they were converted to alkyl-ammonium cations. The obtained isocyanate prepolymers were then extended in the aqueous medium with the use of 1,6-hexamethylenediamine. That yielded stable aqueous dispersions, which were applied on the surfaces of test poly(tetrafluoroethylene) samples. After evaporation of water, the dispersions formed thin polymer coatings. ^{1}H and ^{13}C NMR spectral methods were employed to confirm chemical structures of synthesised cationomers and to modify their quantitative composition in relation to that assumed on the basis of the stoichiometry of the reactions, which were conducted on successive stages of the polyaddition process. Furthermore, the GPC method was used to learn the sizes and distributions of mean molecular weights of those cationomers. Based on ^{1}H NMR spectra, the factor κ was calculated which represented the polarity level of the obtained cationomers. Good correlation was found between that factor and the free surface energy γ_S (increasing in the range 38–42 mJ/m^2) as well as its polar and acid-base components, as determined from the van Oss–Good model on the basis of measured wetting angles between the coatings and model liquids with various polarities. The values of κ and γ_S parameters resulted principally from the increasing amounts of cations NH$^+$, which were evaluated on the basis of the concentrations of tertiary nitrogen atoms increasing within 1.37–2.66 wt%. Those concentrations and amounts resulted, in turn, from the amounts of amine *N*-MDA which could be built into cationomers. The effects were discussed of chemical structures and polarity specifications of polyurethane cationomers on the viscosities of produced aqueous dispersions and on the sizes of their colloidal particles, on the values of free surface energy and on its polar and acid-base components, and on the glass transition temperatures T_{g2} of the rigid segments as found by the differential scanning calorimetry (DSC) method.

Keywords Polyurethane aqueous dispersion ·
Polymer coating · Chemical structure ·
Nuclear magnetic resonance · Polarity · Free surface energy

Introduction

Polyurethane (PU) cationomers are produced chiefly in the reaction of isocyanate-capped prepolymers and low molecular weight tertiary amines, which contain hydroxyl groups in their structures. The suitable ion is obtained when amine is neutralised with acid (acetic acid or formic acid in most cases), or when ammonium salt is formed in the reaction with dimethyl sulfate, alkyl chlorides, benzyl chloride or even with another polymer, which contains chlorine atoms.

Cationomers have the prospects ahead of them which are not any less interesting than those for anionomers, i.e. they can be utilised as waterborne film-forming emulsions [1, 2], coatings, which make glass fibres water repellent [3], materials for electronics (for example, a photosensitive PU coating with built-in stilbene-based chromophores was obtained or bactericidal coatings with structural pirimidynyl groups [4]). Strongly polar cationic groups incorporated into rigid segments of linear PUs considerably improve

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polarity and intermolecular forces within those segments, which contributes to increased phase separation, higher glass transition temperature and melting point of rigid segments, and improved mechanical strength of that polymeric material.

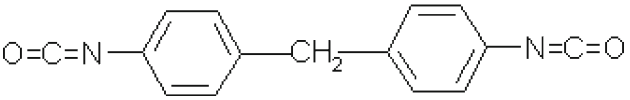
The research work presented in this report was intended to investigate the value of free surface energy (FSE) can be increased by building in more ionic segments derived from *N*-MDA. For this purpose, the selected diisocyanate (MDI), polyoxypropylene glycol (Rokopol 450) and amine (*N*-MDA) were used to synthesise cationomers in the form of aqueous dispersions and thin polymer coatings. The increasing contents of *N*-MDA in successively synthesised cationomers were obtained through a two-stage reaction which yielded isocyanate–urethane prepolymers. The effects of the amounts of ions in cationomers on some physical-mechanical properties were also assessed.

This paper provides an outlook on surface properties of polyurethane cationomers, which is somewhat different from the outlook presented in [5], where the effects were analysed of tertiary nitrogen atoms in polyurethanes, which were synthesised from TDI diisocyanate, poly(tetramethylene) glycol and *N*-MDA. Those polymers were converted into cationomers by quaternisation with alkyl bromides of different chain lengths and then dispersed in water. It was found in [2] that the hydrophilic performance of the polymer was higher in the dispersed state than when cast as a film, which exhibited low critical surface tension values, and that with the increase in chain length of the ioniser and cross-linker, the hydrophobic performance of the cast film increased without the appreciable change in the hydrophilic behaviour of the polymer in the dispersed phase, as can be seen from the interfacial tension and critical surface tension values. In this paper, however, conclusions on polarity of cationomers with the increased amounts of tertiary nitrogen atoms in polyurethanes are drawn directly from chemical structures of those compounds and from surface properties of the coatings obtained therefrom, which are assessed on the basis of their free surface energy values.

Experimental

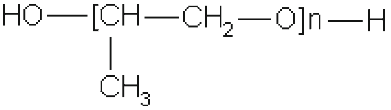
Raw materials and reagents

4,4′-Methylenebis(phenyl isocyanate) (M=250.25 g/mol) (MDI) from Aldrich. The reagent was used as purchased.



(1)

Polyoxypropylene glycol (M_n=450 g/mol), (Rokopol 7P) from the Chemical Factory “Rokita S.A.” in Brzeg Dolny (Poland), (that product was dried under vacuum in nitrogen, at 120°C and during 2 h).



$$HO-[CH(CH_3)-CH_2-O]n-H \tag{2}$$

N-Methyl diethanolamine (*N*-MDA) (Aldrich) (M=119.16 g/mol)

$$(HO-CH_2-CH_2)_2 > N-CH_3 \tag{3}$$

1,6-Hexamethylenediamine (HMDA) from Aldrich (M=116.21 g/mol). The reagent was used as purchased.

$$H_2N(CH_2)_6NH_2 \tag{4}$$

Dibutyl tin dilaureate (DBTL) (from Huntsman Performance Chemicals).

Tetrahydrofurane (THF) (from POCh S.A., Gliwice, Poland).

Formic acid (HCOOH), 99%, analytically pure, (POCh S.A., Gliwice, Poland) (M=46.03 g/mol).

Method for the synthesis of urethane cationomers

Cationomers were synthesised in the glass stand composed of three-necked flask, a heating bowl, a mechanical agitator, a dropping funnel, a thermometer, a reflux condenser and nitrogen a supply nozzle.

As stage 1, urethane–isocyanate prepolymer was synthesised in the reaction of selected diisocyanate (B) and Rokopol 7P (A) (cationomer No. 1):

$$A + 2B \rightarrow AB_2 \tag{5}$$

or MDI (B) and mixture of Rokopol 7P (A) with *N*-methyl diethanolamine (X) (cationomers No. 2–6):

$$nA + mX + qB \rightarrow A_nX_mB_q \tag{6}$$

where $q > n + m$, i.e. this prepolymer will have –NCO terminal groups.

After the synthesis process was completed, the content of free –NCO groups was analysed in the obtained prepolymer. The raw materials and process conditions were carefully selected to maintain the assumed molar ratios of reacting substances at successively carried out process stages (Table 1).

At stage 2, the urethane–isocyanate prepolymer from stage 1 was further reacted with *N*-methyl diethanolamine (X):

$$A_nX_mB_q + pX \rightarrow A_nX_{(m+p)}B_q \tag{7}$$

keeping $q > n + m + p$ at the same time, to build in the additional amount of ionogenic tertiary amine groups to the prepolymer.

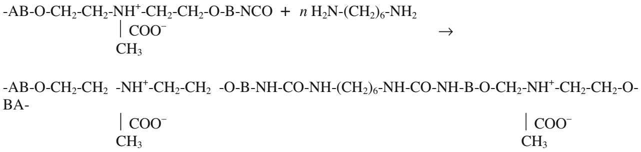
At stage 3, alkyl-ammonium cations were obtained by protonation of tertiary amine groups with HCOOH in the segments to which *N*-methyl diethanolamine was built in:

$$\text{AB-O-CH}_2\text{-CH}_2\text{-}\underset{\substack{|\\ \text{CH}_3}}{\text{N}}\text{-CH}_2\text{-CH}_2\text{-O-BA} + \text{HCOOH} \rightarrow \text{AB-O-CH}_2\text{-CH}_2\text{-}\underset{\substack{|\ \text{COO}^-\\ \text{CH}_3}}{\text{NH}^+}\text{-CH}_2\text{-CH}_2\text{-O-BA} \tag{8}$$

(8)

The number of moles of HCOOH added to the mixture corresponded to the number of moles of built-in tertiary amine ($m + p$), which was present in the known amount of polymer. Table 1 provides weight shares of tertiary nitrogen atom groups in so synthesised cationomers, as calculated from stoichiometry.

Under vigorous agitation conditions, redistilled water with a small amount of HMDA dissolved in it was added at stage 4. The obtained homogeneous dispersion offered pH=2–3 and it contained about 40% polymer. Not only dispersion was formed at this stage, but also those cationomer chains, which contained residual –NCO groups, were subjected to extension:



$$\text{-AB-O-CH}_2\text{-CH}_2\text{-}\underset{\substack{|\ \text{COO}^-\\ \text{CH}_3}}{\text{NH}^+}\text{-CH}_2\text{-CH}_2\text{-O-B-NCO} + n\,\text{H}_2\text{N-(CH}_2)_6\text{-NH}_2 \rightarrow$$

$$\text{-AB-O-CH}_2\text{-CH}_2\ \text{-}\underset{\substack{|\ \text{COO}^-\\ \text{CH}_3}}{\text{NH}^+}\text{-CH}_2\text{-CH}_2\ \text{-O-B-NH-CO-NH-(CH}_2)_6\text{-NH-CO-NH-B-O-CH}_2\text{-}\underset{\substack{|\ \text{COO}^-\\ \text{CH}_3}}{\text{NH}^+}\text{-CH}_2\text{-CH}_2\text{-O-BA-} \tag{9}$$

(9)

Based on expected stoichiometry of successive reactions, the molecular weight M_1 for the repeatable structural unit as well as the contents of tertiary nitrogen atoms N_{III} and total nitrogen N_{total} were calculated for the synthesised cationomers (Table 1).

Analytical methods employed for synthesised cationomers

Determination of nitrogen

The total nitrogen content in polymer coatings was determined with the use of the Elemental Analyser EA 1108 from CARLO ERBA INSTRUMENTS.

Table 1 Chemical compositions of the synthesised cationomers as predicted from the reaction stoichiometry

Sample no.	Stage no.	Substrates					Content of –NCO [wt%]	Content of N [wt%]		Molar weigh of "mer" M_1 [g/mol]
		MDI (B) q	Rokopol 7p (A) n	*N*-MDEA (X) m or p	HCOOH (m+p)	HMDA s		N_{III} (from *N*-MDEA)	N_{total}	
1	1	2.00	1.00	0			8.84	1.19	6.35	1,113
	2			0.95			0.40			
	3				0.95					
	4					0.05				
2	1	3.00	1.00	1.00			6.36	1.99	8.23	1,369
	2			0.95			0.30			
	3				1.95					
	4					0.05				
3	1	5.00	1.00	3.00			4.1	2.49	8.85	2,222
	2			0.95			0.20			
	3				3.95	0.05				
	4									
4	1	7.00	1.00	5.00			3.00	2.81	9.48	2,961
	2			0.95			0.14			
	3				5.95					
	4					0.05				
5	1	9.00	1.00	7			2.38	3.01	9.86	3,699
	2			0.95			0.12			
	3				4.95					
	4					0.05				
6	1	12.12	1.00	10			2.01	3.19	10.22	4,853
	2			1.07			0.09			
	3				11.07					
	4					0.05				

NMR spectroscopy

^{1}H and ^{13}C NMR spectra of the obtained polymers were taken with the use of spectrometer FT NMR Bruker Advance 500II. 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. TMS made the analytical standard.

GPC analysis

Distributions of molecular weights were analysed with the use of the chromatograph Viscotek GPC equipped with the Solvent Pump VE 1121, set of columns (PSS SDV 100 Å+ 1000 Å+Guard) and differential refractometry detector Shodex RI–71. THF was used as the eluent phase. The standard calibration curve, plotted with the use of PS standards, was employed to determine the values of M_w and M_n. The obtained chromatograms were analysed with the use of the original software TriSEC, version 3.0.

Particle size analysis

Sizes of particles in the obtained dispersions were established with the use of the granulometer Mastersizer, type S from Malvern. It was operated and controlled by the software Mastersizer. The measurement was based on recording the radiation intensity of the laser beam which underwent diffraction on colloidal particles.

Viscosity measurements

Viscosity measurements were taken with the use of the rheometer HAAKE-MARS, equipped with the rotor PP 35 (PP = plate–plate).

DSC analysis

Determination of T$_{g2}$ for rigid urethane-urea segments involved the use of the differential calorimeter differential scanning calorimetry (DSC) from Mettler Toledo, type 822^e.

Method for determination of free surface energy components of solids

Measurements of physical parameters of surface energy of solids γ_S, were based on the model by van-Oss–Good, which provides links between the parameters of the free surface energy of solids (S) and of liquids interacting with the former (L) [6, 7]:

$$\left(\gamma_S^{LW}\gamma_L^{LW}\right)^{0.5}+\left(\gamma_S^{+}\gamma_L^{-}\right)^{0.5}+\left(\gamma_S^{-}\gamma_L^{+}\right)^{0.5}=\gamma_L(1+\cos\Theta)/2 \quad (10)$$

where:

Θ experimentally established wetting angle for a liquid drop placed on the studied surface,

$\gamma_{S,L}$ free surface energy value of a liquid (L) or a solid (S), which is a sum of two components:

$$\gamma_{S,L}=\gamma_{S,L}^{LW}+\gamma_{S,L}^{AB} \quad (11)$$

$\gamma_{S,L}^{LW}$ surface energy connected with long-range interactions (dispersion, polar and induction interactions),

$\gamma_{S,L}^{AB}$ surface energy connected with acid-base interactions, as results from the Lewis theory.

One has to remember at the same time that the following consequences for the acid-base component result from the Berthelot theory [4], which assumes that the interactions between the particles of different bodies placed on a surface are equal to the geometric mean of interactions between the particles of each of those bodies:

- for bipolar substances (liquids and solid surfaces), which can be equivalent to synthesised PU ionomers;

$$\gamma_i^{AB}=2\left(\gamma_i^{+}\gamma_i^{-}\right)^{0.5} \quad (12)$$

- for apolar liquid and solid surfaces (diiodomethane, PTFE);

$$\gamma_i^{AB}=0 \quad (13)$$

(where: I = S — solid, L — liquid).

Wetting angles Θ for the obtained cationomer coating surfaces were measured with the use of three model liquids (water, diiodomethane and formamide) with known parameters γ_L, γ_L^{LW}, γ_L^{+}, γ_L^{-} (Table 6). Systems of algebraic Eq. 10 were solved with the use of the computer software MATCAD, and the values of γ_S^{LW}, γ_S^{+} and γ_S^{-} were found for the coatings obtained from the studied cationomers. The values of γ_S^{AB} were calculated from the Eq. 12, while the values of γ_S — from the Eq. 11. The details on the method adopted for taking the measurements can be found in [1].

Results and discussion

Chemical structure of cationomers

The chemical structures of the synthesised cationomers were verified on the basis of H^1 and ^{13}C NMR spectra. Figure 1 shows structural fragments, which make the polymer chains of those cationomers. The exemplary H^1 and ^{13}C NMR spectra for cationomer no. 1 were presented in Figs. 2 and 3, while the detailed interpretations for the spectra of all the analysed cationomers were provided in Table 2. The NMR spectra of the synthesised cationomers were composed of exactly the same signals, while essential differences were observed in signal integration of ^1H NMR, which makes a proof for diversified amounts of built-in segments (Table 3). The spectra confirm the general structures of chains in synthesised cationomers. The presence of urethane structures is proven by the signals, which represent protons *e*, *x* and carbon atoms *C13*, and the ionic structures are represented by the signals corresponding to protons *c*, *z* and carbon atoms *C14*.

Table 4 shows the actual chemical compositions of synthesised cationomers. The molar fractions of rigid urethane segments derived from MDI (q_{exp}), of flexible polyol segments derived from Rokopol 7p (n) and of ionogenic segments derived from *N*-MDA and built in at process stages 1 and 2 jointly $(m + p)_{\mathrm{exp}}$, in relation to 1 mol of Rokopol 7p ($n=1.00$), were calculated from integration data for the proper signals in ^1H NMR spectra (Table 3):

$$q_{\mathrm{exp}} = \frac{I_{\mathrm{arom}} \cdot 3 \cdot 7.46}{I_a \cdot 8} \cdot n \tag{14}$$

where:

I_a, I_{arom} integrations as per Table 3 which correspond to the signals of three protons (*a* type) in group –CH_3 of

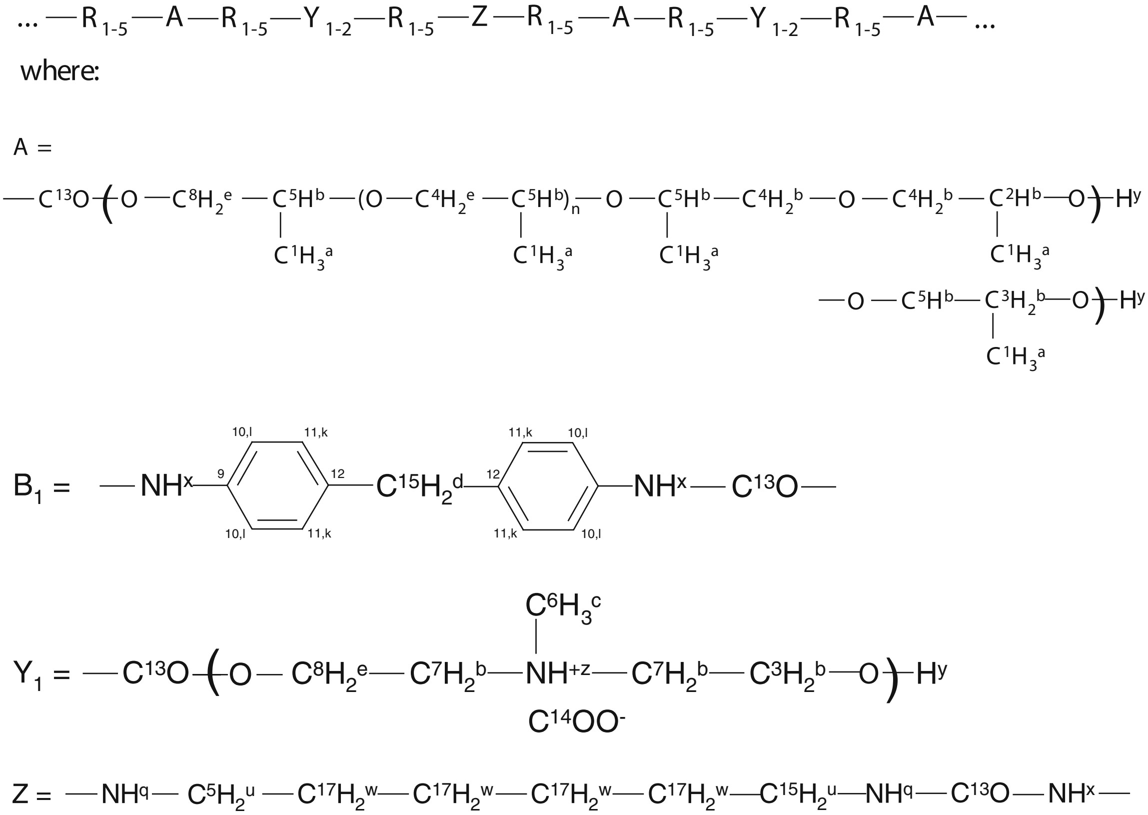


Fig. 1 Chemical structures of synthesised cationomers

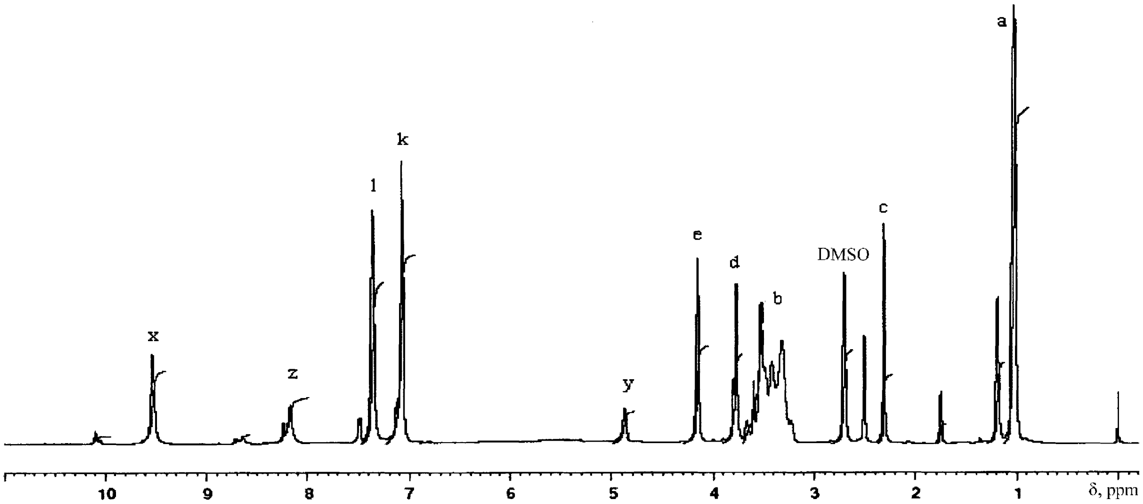
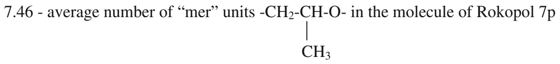


Fig. 2 ^{1}H NMR spectrum of cationomer no. 1 obtained with aromatic diisocyanate MDI and MDEA

Rokopol, and of eight aromatic protons (*k* and *l*) in MDI-derived urethane, respectively;



7.46 - average number of “mer” units $-CH_2-\underset{CH_3}{\underset{|}{CH}}-O-$ in the molecule of Rokopol 7p

(M=450 g/mol);

n=1.00 assumed molar fraction of Rokopol 7p in the cationomer structural unit,

$$(m+p)_{\exp}=\frac{I_c\cdot 7.46\cdot 3}{I_a\cdot 3}\cdot n \tag{15}$$

where:

I_c integration as per Table 3, which corresponds to the signals of three protons (c type).

The molar fraction of built-in rigid urea segments, derived from HMDA ($s_{\exp}$), was calculated from the balance, with the assumption of equimolar ratio of groups – NCO to the total of groups –OH and –NH$_2$ in the final cationomer:

$$s_{\exp}=q_{\exp}-\left[n+(m+p)_{\exp}\right] \tag{16}$$

With the known chemical composition of the cationomer, the molar weight of the structural repeating unit $M_{1\exp}$ was

Fig. 3 ^{13}C NMR spectrum of cationomer no. 1 synthesised with aromatic diisocyanate MDI and MDEA

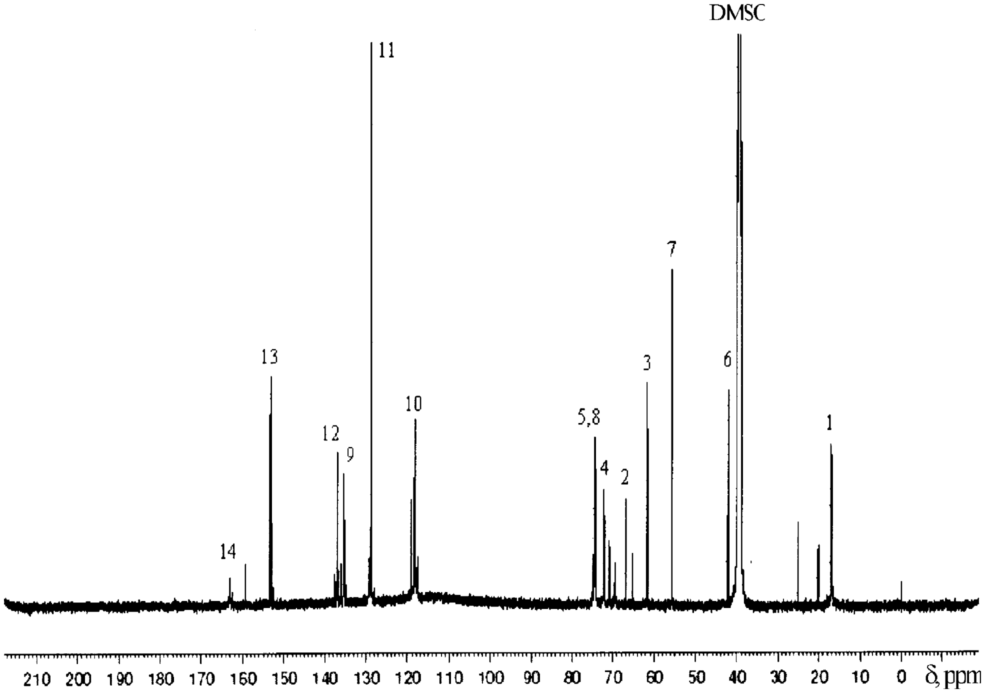


Table 2 Interpretation NMR spectra of the polyurethane cationomer

Type of nucleus	Sample no.					
	1	2	3	4	5	6
	Chemical shifts δ, [ppm]					
	^{1}H NMR spectra					
a	1.03–1.19	1.02–1.32	1.03–1.32	1.02–1.31	1.02–1.31	1.03–1.31
w	1.75	1.75	1.75	1.75	1.75	1.75
c	2.31	2.32	2.30–2.35	2.30	2.30	2.30
DMSO	2.51	2.58	2.55	2.54	2.55	2.54
H_2O in DMSO	2.71	2.70–2.83	2.61–2.79	2.67–2.79	2.68–2.79	2.68–2.79
b	3.23–3.67	3.24–3.67	3.23–3.68	3.23–3.61	3.23–3.80	3.23–3.66
d	3.77–3.80	3.78	3.77	3.77	3.90	3.77
e	4.16	4.15–4.28	4.14–4.16	4.14–4.16	4.14–4.16	4.14–4.15
y	4.87	4.87–4.89	4.87	4.88	4.88	4.87
k	7.07–7.14	7.07–7.09	7.07–7.18	7.07–7.14	7.07–7.18	7.07–7.08
l	7.37	7.36–7.38	7.36–7.37	7.36–7.50	7.36–7.50	7.35–7.37
z	8.17–8.24	8.19	8.24	8.25	8.23	8.21
x	9.54	9.52–9.54	9.54	9.54	9.54	9.54
q					10.12	
	^{13}C NMR spectra					
1	16.77–17.14	16.79–17.15	16.77–17.17	16.77–17.17	16.78–17.21	16.78–17.20
17	25.05	25.07	25.05	25.05	25.05	25.05
DMSO, 15	40.5	40.5	40.5	40.5	40.5	40.5
6	42.16	41.60–42.16	42.11–42.18	42.18	42.17	42.17
7	55.67	55.27–55.68	55.69	55.69	55.68	55.68
3	61.66	60.43–61.65	61.72	61.73	61.71	61.68
2	66.94	66.96	66.94	66.94	66.94	66.94
4	72.09–72.28	72.12–72.31	72.09–72.28	72.11–72.28	72.10–72.29	72.09–72.29
5,8	74.16–74.71	74.18–74.75	74.16–74.72	74.46–74.62	74.16–74.61	74.16–74.59
10	118.23–118.30	118.33	118.20–118.31	118.19–118.31	118.20–118.31	118.20–118.31
11	128.73–128.86	128.11–129.35	128.73	128.73	128.73–128.86	128.73–129.29
9	135.24–135.39	135.26–135.41	135.25–135.38	135.38	135.39	135.38
12	136.99–137.11	137.02–137.15	137.0–137.11	137.00	137.00	136.99
13	153.41	153.43	153.43–153.07	153.43	153.43	152.62–153.42
14	163.18	163.37	163.87	163.95	163.73	163.61

calculated and then one could calculate the amounts of built-in tertiary nitrogen atoms (N_{III}) and total nitrogen atoms (N_{total}):

$$M_{1\,\mathrm{exp}} = 250.25 \cdot q_{\mathrm{exp}} + 450 \cdot n + 119.16 \cdot (m+p)_{\mathrm{exp}} + 46.03 \cdot (m+p)_{\mathrm{exp}} + 116.21 \cdot s_{\mathrm{exp}} \qquad (17)$$

$$N_{\mathrm{III}} = \frac{14 \cdot (m+p)_{\mathrm{exp}}}{M_{1\,\mathrm{exp}}} \cdot 100\% \qquad (18)$$

$$N_{\mathrm{total}} = \frac{14 \cdot \left[(m+p)_{\mathrm{exp}} + 2\left(q_{\mathrm{exp}} + s_{\mathrm{exp}}\right)\right]}{M_{1\,\mathrm{exp}}} \cdot 100\% \qquad (19)$$

When comparing the data presented in Tables 1 and 4, one can notice certain differences between the quantitative compositions, which can be expected for the synthesised cationomers from the assumed stoichiometry and their actual compositions established from the analysis of NMR spectra. Yet, the adopted general course for obtaining successively higher and higher ion contents in the produced cationomers, which result from the presence of tertiary nitrogen atoms (N_{III}) derived from *N*-MDA, remains maintained. That is the consequence of the growing molecular weight of the structural repeating unit M_1 and of the growing content of total nitrogen atoms (N_{total}) in the cationomer molecule. The latter is additionally confirmed by the findings from the determinations of the total nitrogen contents by the elemental analysis method (Table 4). The increasing fractions of HMDA-derived segments in relation to the flexible ones

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

Sample no.	1	2	3	4	5	6
	Integration (conventional unit)					
I_b	2.2206	2.3880	1.4361	1.1676	1.0781	1.022
I_c	0.3626	0.4282	0.5539	0.6064	0.6055	0.6122
I_e	0.5139	0.6120	0.7455	0.8307	0.8217	0.8546
I_y	0.1712	0.1632	0.0845	0.0585	0.0531	0.0485
I_z	0.2449	0.3180	0.2734	0.2684	0.2782	0.2803
I_x+I_q	0.4753	0.4558	0.4754	0.4759	0.4628	0.4711
I_P	3.9885	4.3652	3.5688	3.4075	3.2994	3.2887
I_a	2.2051	1.8823	1.1351	0.8615	0.6611	0.5357
I_h	0.1023	0.4881	0.3438	0.3975	0.4797	0.5181
I_d	0.4707	0.4853	0.4570	0.4551	0.4754	0.4733
I_{arom}	1.8543	2.0831	1.9698	1.9581	1.9278	1.9518
I_N	4.6324	4.9388	3.9057	3.6722	3.544	3.4789
κ	46.27	46.92	47.75	48.13	48.26	48.59
I_c/I_a	0.1644	0.2184	0.4149	0.7039	0.8072	0.9962
I_c/I_d	0.7703	0.8823	1.1220	1.3325	1.2737	1.2935

derived from Rokopol 7p and rigid urethane segments is also proven by the increasing values of the integration ratios I_c/I_a and I_c/I_d (Table 3). Interesting enough is the increased fraction of urea-derived segments (s_{exo}) in relation to the value of (s) (Tables 1 and 4), which shows that the amount of urethane-urea chains formed at the synthesis stage 4 through chain extension with the use of HMDA is higher than expected.

The average molecular weights M_w and M_n, determined by the GPC method and calculated from the polydispersity degrees (Table 4):

$$P = \frac{M_w}{M_n} \tag{20}$$

demonstrate that the adopted method of multi-stage polyaddition does not yield the cationomers with unambiguously increasing molecular weights. The average molecular weights, determined for cationomers 2–5, turned out close to each other, and the polydispersity degree P was similar for all the cationomers, as shown by the distribution curves presented in Fig. 4. When, however the fact is considered that—as pointed out above—the sizes of the structural repeating units ("MERs") M_1 increase for the successive cationomers, the synthesised cationomers are characterised by the diversified degree of polymerisation DP (Table 4):

$$\text{DP} = \frac{M_w}{M_{1\,\text{exp}}} \tag{21}$$

Thus, the suggested method of multistage polyaddition makes it possible to produce cationomers with the increasing contents of ionic segments, but the sizes of

Table 4 Chemical compositions of synthesised cationomers

Sample no.	Substrates				Content of N [wt%]		Molar weight of "mer" $M_{1\text{exp}}$ [g/mol]	Total N [wt%]	M_w [g/mol]	M_n [g/mol]	M_w/M_n [g/mol]	DP	HS [wt%]	T_{g2} [°C]
	MDI q_{exp}	Roko-pol 7p (A) n	N-MDEA (X) $(m{+}p)_{\text{exp}}$	HMDA s_{exp}	Tertiary N (from N-MDEA) (N_{III})	Total N (N_{total})								
	by ^{1}H NMR							By elemental analysis	by GPC			By ^{1}H NMR and GPC	By ^{1}H NMR	By DSC
1	2.35	1.00	1.23	0.12	1.37	6.90	1256	6.67	8,800	4700	1.87	7.00	64.2	16
2	3.10	1.00	1.70	0.40	1.53	7.84	1553	7.64	22,100	13,300	1.67	14.24	71.0	19
3	4.85	1.00	3.64	0.21	2.25	8.50	2268	8.41	27,700	12,400	2.24	12.22	80.2	27
4	6.37	1.00	5.25	0.12	2.51	8.72	2925	8.69	25,700	14,100	1.82	8.77	84.6	25
5	8.13	1.00	6.83	0.30	2.62	9.09	3648	8.93	26,500	13,800	1.92	7.26	87.7	20
6	10.2	1.00	8.53	0.67	2.66	9.44	4489	8.78	39,800	22,900	1.74	8.86	90.0	27

Experimental values calculated from ^{1}H NMR spectra, elemental analysis and from GPC methods individual macromolecules generally do not grow up; distributions of their molecular weights remain similar as well. The values obtained for DP and for the contents of tertiary nitrogen atoms demonstrate that those cationomers should be classified as urethane-urea oligomers, which contain firmly built-in cations R_3NH^+ derived from HMDA and HCOOH, neutralised with formate anions, which made it possible to produce stable aqueous dispersions with about 40% of dispersed solid polymer phase.

The observed decline in viscosity versus the rate of shear (Fig. 5) justifies the obtained dispersions to be classified as pseudoplastic liquids. The viscosity values increase for the dispersions of the successive cationomers, which is most probably caused by the increasing ionic interactions due to the growing number of ions that have been built in. Within the increasing rate of shear of 20–30 s^{-1}, however, a sharp decline in viscosity is observed for the studied dispersions, which can be accounted for by the mechanical damage of the structures of polymer balls and dispersion particles.

The observed viscosity performance was also affected by the increasing size of particles in the produced dispersions, as can be concluded from the data presented in Table 5. However, the character of the particle size distribution was diversified, as illustrated by the charts in Fig. 6. Yet, about 90% of all agglomerates in any dispersion fell within 1–100 μm on the average. Sedimentation of the produced dispersions was thus relatively slow, which means that they were stable under storage conditions.

After the obtained aqueous cationomer dispersions were applied to the apolar surface of poly(tetrafluoroethylene) (PTFE, type TARFLEN) and water was expelled from them by air drying at 20°C, thin polymer films were produced which were subjected to seasoning at the same conditions for another 10 days. Polarity of coatings so obtained was studied by finding the wetting angles with the use of three model liquids. The angles were then utilised to calculate the free surface energy values γ_S and its components: γ_S^{LW}, γ_S^+ and γ_S^- (Table 6), from the van-Oss–Good model (Eq. 10) The wetting angles as measured and the components of free surface energy as calculated from said angles for the cationomer coatings were provided in Table 7. The obtained polyurethane coatings have the free surface energy

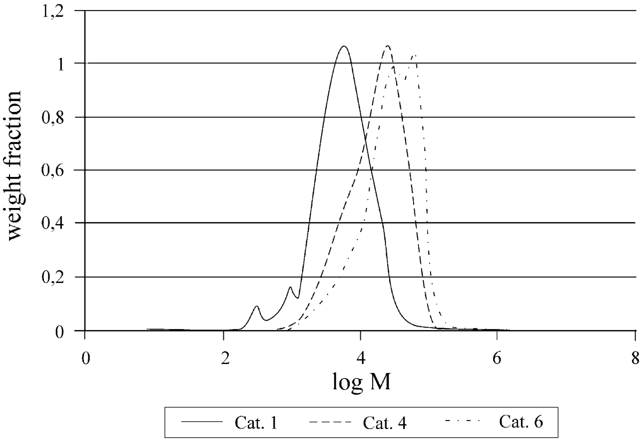


Fig. 4 MWD curves for cationomers no. 1, 4 and 6

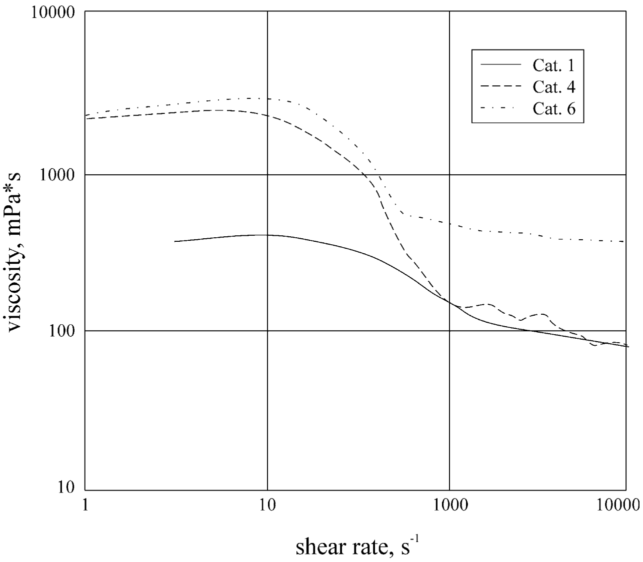


Fig. 5 Curves for dynamic viscosity versus the rate of shear in aqueous dispersions of cationomers no. 1, 4 and 6

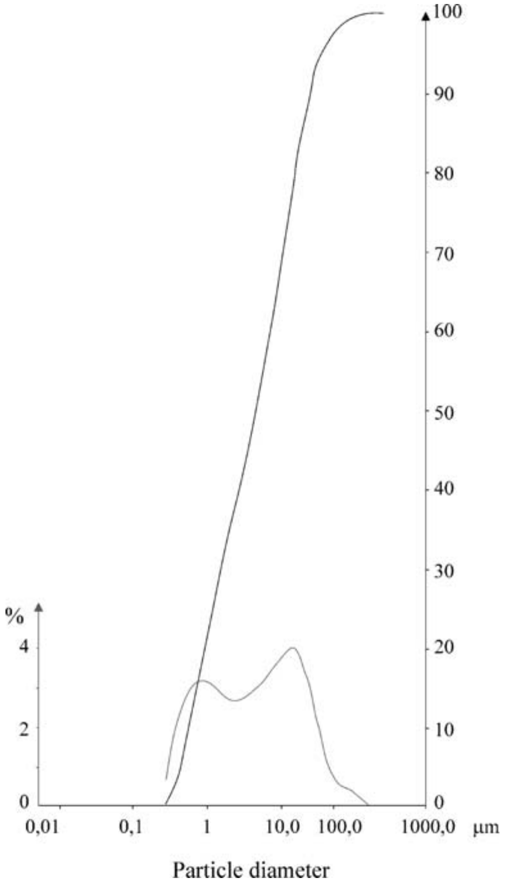


Fig. 6 Molecular size distribution curves for aqueous dispersions of cationomers no. 1, 4 and 6

Table 5 Sizes of cationomer particles in aqueous dispersions

Sample no.	Particle size [μm]	Share [%]
1	0.53–10.00	52.50
	10.62–100.00	47.50
3	0.53–10.00	50.43
	10.62–80.14	44.00
	51.15–169.40	5.57
4	0.53–10.00	14.73
	10.62–100.30	44.3
	108.1–169.00	40.97
5	0.53–10.00	16.04
	10.62–100.00	73.55
	108.000–169.00	10.41
6	0.53–3.46	4.24
	10.62–169.00	95.76

value generally γ_S>43 *m*J/m^2, which classifies them as medium-polarity materials.

The observed clear increase of FSE for coatings 1–6 results from their increasing amounts of polar urethane and urea segments. Those segments were introduced to the cationomer chains by extending prepolymers at stages 1 and 2 through adding more and more *N*-MDA. That idea yields higher polar and dispersion interactions, which is manifested by the values of the component γ_S^{LW}. Developing the cationomer structure by extension of isocyanate prepolymers with amines (*N*-MDA) and with HMDA at the final stage shall obviously contribute to the formation of a richer structure of hydrogen bonds, which shall additionally enhance polar interactions.

In addition, γ_S^{AB}, and in particular the component representing the base interactions γ_S^-, which are typical especially for aliphatic amines, goes to higher values for the cationomer coatings considered and it increases from 6.0 to 34 mJ/m^2 with the increasing shares of ionic structures. Adding more cations R_3NH^+ and their neutralisation with counter-ions COO− results, as can be seen, in the general increase of free surface energy γ_S. That increase is not caused solely by the increasing component γ_S^{LW}, but the component γ_{S^-} is also found to add its contribution. Modifications of cationomer chain structures, which are characterised—as shown by NMR analyses—by the increased amounts of tertiary nitrogen atoms from 1.37 to 2.66%, make the effective way of increasing the free surface energy values of the coatings obtained from those cationomers from about 43 to 50 mJ/m^2.

Table 6 Surface properties of model measuring liquids [4]

Model measuring liquids	Free surface energy parameters [mJ/m^2]				
	γ_L	γ_L^{LW}	γ_L^{AB}	γ_L^-	γ_L^+
Water	72.8	21.8	51	25.5	25.5
Formamide	58.0	39.0	19.0	39.6	2.28
Diiodomethane	50.8	50.8	0	0	0

To confirm additionally the supposition that the growth of the free surface energy comes from the polar nature of the successive cationomers, the attempt was made to define the correlations (qualitative correlations only at this stage of our study) between the free surface energy parameters and polarity of cationomer structures as established from ^{1}H NMR spectra. The factor was calculated for that purpose:

$$\kappa = \frac{I_P}{I_P + I_N} \cdot 100\% \tag{22}$$

where:

$$I_P = \sum \left(I_b + I_c + I_e + I_y + I_z + I_x + I_q\right) \tag{23}$$

makes the sum of integration of signals for protons of the group N–CH$_3$ (c), signals recorded over a wide band of δ= 3.0–5.0 ppm (designated as *b*, *e*) and originated from groups CH$_2$ and CH connected to polar ether groups, to nitrogen atoms, to groups –OH, to urethane or urea groups, signals of protons of residual groups –OH (*y*) and polar groups NH in urethanes, urea compounds and allophanates (*x*, *q*), and of protons (*z*) of imine group R_3NH^+, which has been neutralised with the formate anion COO$^-$, while:

$$I_N = \sum \left(I_a + I_w + I_d + I_k + I_l\right) \tag{24}$$

is the sum of integration of signals for protons of apolar groups −CH$_3$ in Rokopol 7p (*a*), of the bridge group CH$_2$ in MDI diisocyanate (*d*) and groups CH$_2$ type (*w*) in amine chain extender HMDA, and signals of aromatic protons in MDI (*k, l*).

With that assumption, Eq. 23 presents the value which is proportional to the amounts of chemical structures with the dominant effect on polar interactions, and Eq. 24 represents non-polar interactions in the structures of synthesised cationomers (Fig. 1). One may assume then that the value of the factor κ as calculated from Eq. 22 makes the physical characterisation of the polarity degree of a given cationomer. The data presented in Table 3 show that the values of the factor κ for the series of synthesised cationomers vary within 46.3–46.6%, which can be declared a small difference in the light of previous investigations. Thus, that factor may be recognised as a reliable measure of the polarities of the synthesised coatings, compliant with the values of γ_S as regards the route of changes.

Another important parameter, which characterises mechanical–thermal properties of polymer coatings, is the glass transition temperature T_g. Two temperature values are

Table 7 Comparison of determined contact angles calculated values of free surface energy components of the synthesized polymer cationomers

Average contact angle Θ [°] (SD)				Free surface energy components [mJ/m^2]				
Sample no.	Model measuring liquids			γ_S^{LW}	γ_S^+	γ_S^-	γ_S^{AB}	γ_S
	Diiodo-metha-ne	Form-amide	Water					
1	30.65	48.69	73.75	38.414	0.828	6.042	4.473	42.887
	1.37	1.59	1.11					
2	28.99	45.74	72.34	39.011	1.077	6.019	5.092	44.103
	0.70	0.91	1.36					
3	27.32	42.08	64.32	39.586	0.937	11.592	6.591	46.177
	0.99	0.42	1.32					
4	24.45	38.53	52.26	40.508	0.542	23.426	7.127	47.635
	0.47	0.40	0.45					
5	22.46	37.39	44.12	41.096	0.277	33.173	6.063	47.159
	0.55	1.05	1.08					
6	17.52	31.73	40.72	42.364	0.457	33.675	7.8846	50.210
	0.44	1.17	1.26					

usually specific for polyurethane elastomers: they represent vitrification of flexible segments $T_{g1}<0$ and of rigid segments $T_{g2}>0$. Figure 7 shows the DSC thermograms recorded for cationomer no. 6. Table 4 provides the values of T_{g2} for urethane and urea hard phases present in the studied cationomers and weight fractions for those segments (HS) as calculated from ^{1}H NMR spectra:

$$HS = \frac{250.25 \cdot q_{\exp} + 119.16 \cdot (m+p)_{\exp} + 46.03 \cdot (m+p)_{\exp} + 116.21 \cdot s_{\exp}}{M_{1\,\exp}} \cdot 100\% \tag{25}$$

The weight fraction of the hard phase in the synthesised cationomers is considerable, and with the increasing amounts of ionic, urethane and urea segments incorporated into those structures, it also increases gradually from 64 to 90%. The soft phase is composed solely of the segments, which are derived from Rokopol 7p. That gives the increase in T_{g2} of hard segments (observed by DSC) within the range of 15–27°C. Other investigations show that the glass transition temperature of soft polyether segments (T_{g1}) derived from polyoxypropylene glycol, not observed in those measurements, amounts to about −60°C [8]. The observed increase in T_{g2} should be accounted for not only

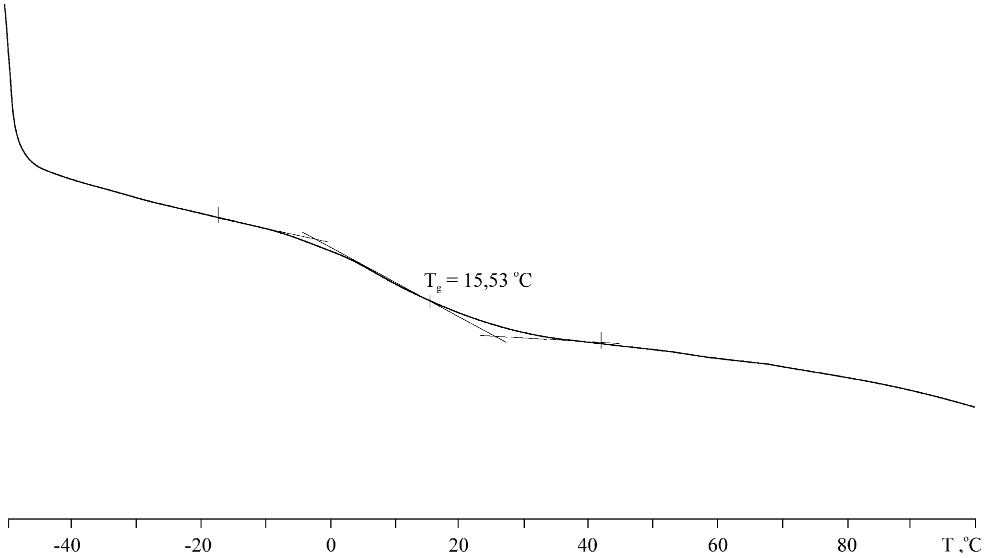


Fig. 7 DSC thermogram for cationomer coating no. 1

by the increasing fraction of the hard phase but mainly by changes in its arrangement, which probably results from the increasing share of ionic, urethane and urea structures, which form stable hydrogen bonds.

Conclusions

The multistage synthesis method, which has been developed and which consists in gradual extension of urethane–isocyanate prepolymers with the use of *N*-MDEA to produce cationic centres NH^+ neutralised with counter-ions COO^-, and [which consists in] termination of prepolymers containing residual –NCO groups in the reaction with HMDA, [the method] yields aqueous dispersions of polyurethane cationomers. These, after evaporation of water, make it possible to form thin polymeric coatings on poly(tetrafluoroethylene) surfaces. When the amounts of incorporated amine *N*-MDEA are controlled, cationomers can be produced with increased fractions of cationic segments. Analyses of ^{1}H NMR spectra have shown that the structures of produced cationomers are different from those expected from the stoichiometry, despite the carefully selected ratios of reacting substances at successive process stages. In particular, at the final process of cationomer dispergation in water with the addition of HMDA, considerable amounts of that amine become built in, which contributes to additional stiffening of the structure by urea segments. As results from the investigations by the GPC method, the average molecular weights of the synthesised cationomers do not increase very much, although the molecular weight M_1 of the repeatable structural unit increases because more and more groups R_2NH^+ are built into the structure. The obtained cationomers should be classified as oligomers with the degree of polymerisation equal to DP=7–14. Also, their polydispersity of P=1.7–2.2 is not dependent on the amounts of built-in ionic segments. However, the increasing amounts of urethane segments, urea segments and ionic groups is responsible for the noticeable growth in polarity, as characterised by the factor κ, calculated from ^{1}H NMR spectra. There is a good correlation between that factor and the growing value of free surface energy γ_S, and with its components γ_S^{LW} and γ_S^-, as well as with the changes in the structures of hard segments, which manifest themselves by the growth of T_{g2}. That can be accounted for by the increased content of structures, the formation of which is favoured by relatively numerous hydrogen bonds.

In general, the research programme was conducted, which made it possible to learn the influence of the production method on the physical–chemical properties. Further investigations are expected to yield the empirical correlation(s) between the factor κ, which is representative for cationomers and which is calculated on the basis of ^{1}H NMR spectra, and free surface energy values of cationomers. Those correlations will then be helpful in the production of many valuable materials, e.g. polyurethane medical implants, for which the properties are controlled by polarity of their molecular structures and hence they can be predictable on the basis of the reactant volumes employed at successive stages of the polyaddition process.

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