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ORIGINAL CONTRIBUTION

**Piotr Król**
**Bożena Król**
**Stanisław Pikus**
**Maciej Kozak**

# Polyurethane anionomers synthesised with aromatic, aliphatic or cycloaliphatic diisocyanates, polyoxyethylene glycol and 2,2-bis-(hydroxymethyl)propionic acid. Part II. Supermolecular structure. Thermal properties

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P. Król (✉) · B. Król
Department of Polymer Science,
Faculty of Chemistry, Rzeszów
University of Technology,
Al. Powstańców Warszawy 6,
35-959 Rzeszów, Poland
e-mail: pkrol@prz.rzeszow.pl

S. Pikus
Faculty of Chemistry,
Maria Curie-Skłodowska University,
Lublin, Poland

M. Kozak
Department of Macromolecular
Physics, Adam Mickiewicz University,
Poznań, Poland

**Abstract** Small angle X-ray scattering and differential scanning calorimetry methods were employed to characterise the internal order of structural phases present in polyurethane coatings obtained as a result of water evaporation from anionomer dispersions. Those anionomers were produced in the reaction of aromatic, cycloaliphatic and aliphatic diisocyanates with polyoxyethylene glycol, 2,2-bis-(hydroxymethyl)propionic acid and 1,6-hexamethylenediamine. The decisive effects were found from ionic and polar structures within the rigid urethane and urea segments on the ordered arrangement degree of the supermolecular structures in the obtained anionomers. That becomes apparent in differential scanning calorimetry thermograms and contributes to improved thermal stability of the produced polyurethane coatings.

**Keywords** Polyurethane anionomers · Polarity of bonds · Segmented structure · DSC · SAXS · Thermal decomposition

## Introduction

Part 1 of this work [1] described the synthesis and molecular structures of polyurethane (PU) anionomers obtained from various diisocyanates, polyoxyethylene glycol and 2,2-bis-(hydroxymethyl)propionic acid and which were then extended in the aqueous medium by means of 1,6-hexamethylenediamine. The possibility was outlined of utilising so produced aqueous dispersions as environmentally friendly polyurethane lacquers and as binding agents for powdered metal oxides to be employed in the manufacture of ceramic ware. The chemical structures of so obtained anionomers, which contained about 2 wt% of dissociable $COO^-$ groups, were strongly diversified within the rigid polar urethane structures as those anionomers were derived from diisocyanates with various chemical structures. Moreover, as revealed in generalised phase contrast tests, considerable differences in reactivity of –NCO groups present in diisocyanate feedstocks resulted in diversified average molecular weights of the synthesised ionomers. Hence, one can expect that strong interactions within rigid urethane segments and flexible polyol–ether segments, resulting from structural polarity, ionic interactions and intermolecular hydrogen bondings, would affect the morphological features of the condensed phases of anionomers. These factors may cause the polymer chains organising in the supermolecular structures with a defined crystallographic order, which occur in the separate phase regions made from rigid and flexible segments. During creating such an ordering, the way of polymer coating formation plays an important role. This ordering determine the use of the 'supermolecular structure' expression in the title of the present study. These supermolecular structures are created spontaneously and additionally diversify the synthesised anionomers. They can consequently affect the thermal and electrical proper-

ties of the new coating materials obtained from polyurethane anionomers. These questions have been addressed in this paper, while the electrical properties will be discussed in part 3 of our study.

## Experimental

### Materials

Polyurethane anionomers [1]:

- PU anionomer obtained from the reaction of 2,4- and 2,6-tolylene diisocyanate (2,4- and 2,6-TDI), polyoxypropylene glycol ($M_n$=450 g/mol) (Rokopol 7p) ($M_n$=450) and 2,2-bis(hydroxymethyl)propionic acid (DMPA), neutralised with triethylamine (TEA) and extended by means of 1,6-hexamethylenediamine (HMDA); that anionomer offers the increased content of ions (2.26 wt% $COO^-$, sample no. 1)
- PU anionomer obtained in the same way from 4,4′-methylenebis(phenyl isocyanate) (MDI), (1.95 wt% $COO^-$, sample no. 2)
- PU anionomer obtained from 4,4′-methylenebis(cyclohexyl isocyanate) (HMDI), (1.91 wt% $COO^-$, sample no. 3)
- PU anionomer obtained from isophorone diisocyanate [5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane] (IPDI) (2.06 wt% $COO^-$, sample no. 4)
- PU anionomer obtained from 1,6-diisocyanathexane (HDI) (2.29 wt% $COO^-$, sample no. 5)

The test coatings of synthesised anionomers were obtained by conservative evaporation of water from aqueous dispersions applied to polytetrafluoroethylene panels in a drier ($T$=110 °C, $t$=60 min).

### Testing equipment and analytical methods

#### *SAXS analysis*

The scattering measurements were conducted with the use of the NanoSTAR system (Bruker AXS) provided with the pinhole collimation and the two-dimensional detector (HiSTAR) mounted on the micro focus X-ray tube with the copper anode and equipped with the crossed Göbel mirrors.

The sample-to-detector distance was 650 mm. The exposure time for a single frame was 10,000 s. All measurements were performed at room temperature. Taking into account the external appearance of the investigated samples, the small angle X-ray scattering (SAXS) measurements were taken a few times for different parts of the same sample.

#### *Differential scanning calorimetry*

A Mettler Toledo type 822® differential calorimeter with STAR® System software was employed to analyse the thermal properties of cured PUs. The instrument was calibrated with the use of Zn and In standards.

The samples were placed in aluminium crucibles. These were weighed to the nearest 0.0001 g and placed in the measuring chamber. The samples were initially heated up to 60 °C to eliminate stresses which could possibly be left after the moulding process, and then they were cooled down to −80 °C. After another 10 min, their progressive heating was initiated at the rate of 10 °C/min. The measurements were taken within the temperature range from −70 to 100 °C, in an environment of nitrogen passed at the rate of 30 $cm^3$/min.

In case of anionomer nos. 2 and 3, additional measurements were taken with the use of the Instrument Netzsch DSC 200, within the temperature range −100 to 100 °C (heating rate 10 K/min).

#### *Thermogravimetric analysis*

Thermal stability of the synthesised anionomers was investigated by thermogravimetric analysis (TG). The determination utilised a F. Paulik, J. Paulik, L. Erdey derivatograph from MOM (Hungary). Samples at 100 mg were held at 20–900 °C over 100 min and mass decrements were recorded against temperature. The derivative thermogravimetry (DTG) and differential thermal analysis (DTA) curves were recorded at the same time.

## Results and discussion

The SAXS scattering curves for the investigated anionomer samples are presented in Fig. 1. as log $I(q)$ vs log $q$ [where $I(q)$ scattering intensity, $q$ scattering vector for which the modulus is equal: $q=(4\pi\sin\theta)/\lambda$, $2\theta$ scattering angle, $\lambda$ wavelength of CuK$\alpha$]. The investigated anionomers have relatively low X-ray absorption which allows for the use of relatively thick samples in SAXS measurements. Thus, the measured SAXS intensity values originate from relatively big sample volumes and they can be treated as good representative average values for the investigated anionomers. Nevertheless, it should be noted that, for some samples, small differences in SAXS results measured in different parts of the sample were observed.

The SAXS curves for individual anionomers (Fig. 1) differ clearly from each other in shape (run) as well as they show different levels of intensity. It is worth remembering that the run (shape) of SAXS curves depends on the shape, sizes and degree of ordering of the scattering objects (i.e. regions with different electron densities), while the level of intensity results from the amount of existing scattering

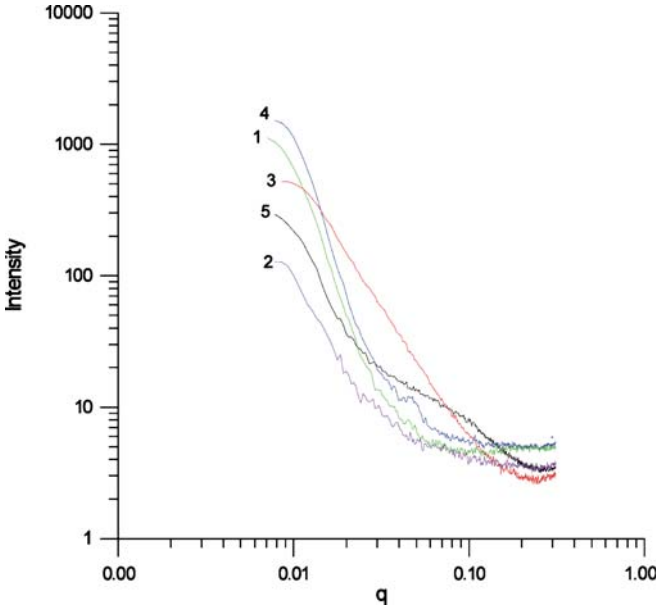


**Fig. 1** SAXS spectra for polyurethane anionomers no. 1–5

objects and it strongly depends on the difference in the electron density between the scattering objects and their surroundings.

The SAXS curve for anionomer no. 3, which was synthesised with the use of HMDI and the structure of which was classified as weakly polar (by the rules adopted in part 1 of this paper [1]), fulfilled as the only one with the scattering power law $[I(q) = I_o q^{-\alpha})$ in the broad range of scattering vector $q$ [2]. It means that the structure existing in this sample can be treated as the mass fractal system probably built of hard urethane–urea segments strengthened by additional electrostatic interactions of active ions species ($COO^-$ groups and counter ions which are formed by ammonia cations derived from TEA). For this anionomer, small differences in the profile of the SAXS curves measured at different parts of the sample are observed; the feature can be explained by forming some additional heterogeneities in supermolecular structures when the coating of anionomer is formed. The presence of the mass fractals in the condensed coating phase of the ionomer indicates the existence of the limited but distinct ordering of the phases which were formed by the water evaporation process from the polymer dispersion deposited on the carrier with heterogeneous local surface energy. That is considered possible as some differences in the wetting angles were observed in the past even for the standard liquids when placed on polar polymeric surfaces, for example, on polyethyleneterephthalate [3].

Sample no. 5, synthesised from HDI, which was shown to have the relatively highest polarity [1], also demonstrates some kind of ordering, as is suggested by the presence of the broad peak for $q$=0.1 on the SAXS curve. The relatively low intensity of that peak and its visible broadening can suggest the non-uniform dispersion of the hard segments in the space, causing the degree of ordering of this sample to be described as rather low [4]. The precise mathematical analysis of the location of the peak maximum indicates that the value of the long spacing $L$ for anionomer no. 5 is equal to about 58–70 Å, depending on the place in the sample.

Sample no. 4, synthesised from IPDI, which was classified as the sample with the lowest polarity [1], shows on SAXS curves a much more narrow peak at the lower value of $q$ than the peak for the sample no. 5; the obtained value of the long spacing $L$ for this sample places the $L$ parameter within 132–170 Å. It suggests better separation of hard segments than in the sample no. 5 and better organisation in greater hard domains. The similar value of the linear parameter ($d$=179 Å) was obtained by SAXS measurements for the urethane–acrylic copolymer structure. The value $d$=179 Å was described [5] as the characteristic interdomain spacing, existing in the hard domain formed from orderly arranged hard segments.

The SAXS curves of aromatic anionomers (samples no. 1 and 2), which were synthesised from DMI and TDI diisocyanates, respectively, and the structures of which were described as polar ones [1], do not show – unexpectedly – any clear features which would indicate the existence of ordering in these samples. Sample no. 1 has weak SAXS scattering for higher values of scattering vector $q$ (see Fig. 1.). It means that this anionomer has a much lower number of bigger-sized electron density heterogeneities than the other ones. It can be explained by a relatively good dispersion of the hard segments in the generally soft polymer matrix.

## Interpretation of DSC thermograms

Figure 2 presents the differential scanning calorimetry (DSC) thermogram (recorded with the use of the thermoanalyser Metler Toledo STAR System) for the anionomer no. 2 sample, synthesised from MDI. Before the heating process, the sample was kept at −70 °C over 10 min. Between the temperatures −70 and 100 °C, the phase change can be observed within −60 to −70 °C, which is attributable to glass transition of soft polyether segments on the background of typical changes in thermal capacity of the studied system; above the temperature of 0 °C, the phase change represents glass transition of rigid urethane–urea segments. The mathematical analysis of the obtained curve made it possible to formally assign the value of $T_{g_1} = -69\,^{\circ}C$ to flexible segments and the value of $T_{g_2} = 49\,^{\circ}C$ to rigid segments. The difficulties faced when we attempted to provide interpretations for the obtained thermograms made us repeat the measurement with the use of the Netzsch DSC 200 instrument—the measurement was taken independently and the amount of sample no. 2

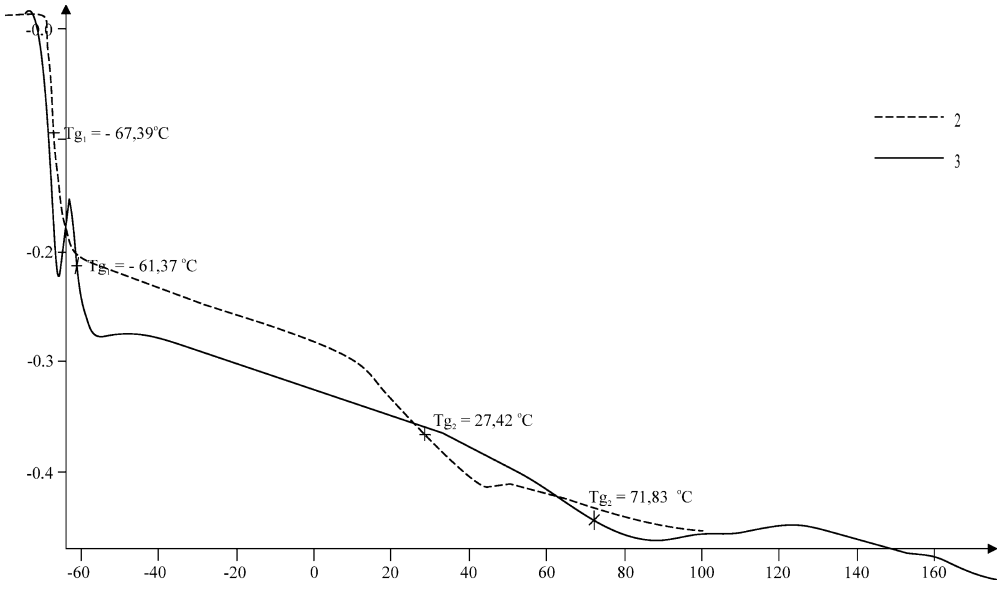


**Fig. 2** DSC thermograms for polyurethane anionomers nos. 2 and 3 analysed on the Metler Toledo calorimeter

was lower. That thermogram was presented in Fig. 3. In the 'below-zero' range, a poorly outlined transition can be observed in this thermogram at $T_{g_1} \approx -69\,^{\circ}C$ , while at least two phase transition points are visible in the 'above-zero' range at $T_{g_2} \approx 10$ and 63 °C. Hence, the profiles of those two thermograms, taken with the use of two DSC instruments, match better at negative temperatures. The two glass transition points observable within positive temperatures can be formally attributed to phase transitions of rigid urethane segments derived both from aromatic diisocyanate MDI and low molecular weight ionogenic compound DMPA; the latter is additionally bonded ionically with the TEA-derived ionic pair which has been built in into the polyurethane chain and with the urea segment derived from HMDA introduced at the synthesis final stage as the polyurethane chain extension agent.

Similar comparative measurements were taken with the use of both of these instruments for sample no. 3 which had been synthesised from hydrogenated diisocyanate HMDI. The obtained thermograms were presented in Figs. 2 and 3. After analysing those curves, we could link the values of $T_{g_1} \approx -62\,^{\circ}C$ and $T_{g_2} = 72\,^{\circ}C$ (Metler Toledo STAR System) as well as $T_{g_1} = -30\,^{\circ}C$ and $T_{g_2} = 50\,^{\circ}C$ (Netzsch DSC 200) to the observed changes. The differences in findings obtained by the two DSC instruments can be explained solely by the inhomogeneity of phase

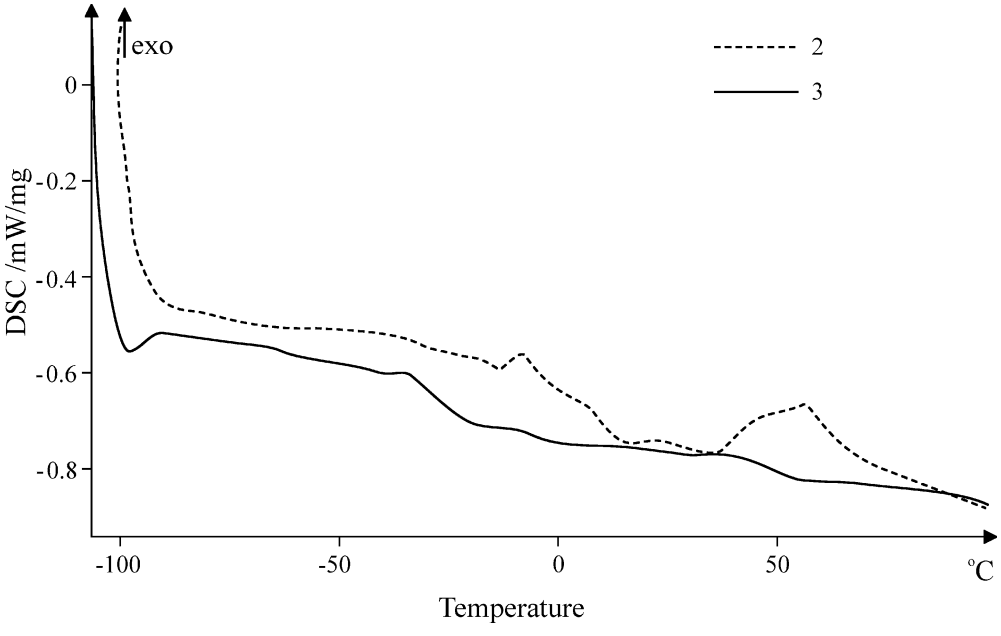


**Fig. 3** DSC thermograms for polyurethane anionomers nos. 2 and 3 analysed on the Netzsch DSC 200 calorimeter

structures in the material taken for tests from different locations of the same sample. (As discussed earlier, structural inhomogeneity of tested materials was also found when SAXS diffraction patterns obtained for various places within the same sample were compared to each other.) Hence, the remaining anionomer samples were analysed solely with the use of Metler Toledo STAR System and bigger samples were taken for tests (about 100 g) so that the findings can be considered more reliable (Table 1). As results from the presented data, the DSC measurements made it possible to provide the rough values only of the upper and lower glass transition temperatures. On the other hand, there is no doubt that phase separation took place in the studied anionomers. Its extent was different for individual samples of anionomers, and it was even different at various locations within the same sample, which was confirmed by the analysis of the SAXS curves. That phenomenon relates predominantly to the phase of rigid segments. The DSC profile of sample no. 5 within the temperature region of glass transition of rigid segments was different from that of other profiles. No transition was observed for that sample within positive temperatures, which suggests that we deal with a polymer which is generally an elastomer, wherein two 'negative' glass transition temperatures are observed, with $T_{g_2} < 0\ ^\circ C$ referring to the glass transition of relatively flexible urethane segments created from aliphatic HDI.

Thermal stability of synthesised anionomers

The information on thermal stability of synthesised anionomers was derived from thermogravimetric analyses (TG and DTG) and from the DTA curves which were recorded at the same time. The temperature $T_{DTG\min}$, at which the higher mass loss is observed was assumed a criterion for comparison of thermal stability of the tested samples. However, the results from thermograms of sample no. 1, shown in Fig. 4, indicate that this factor is unable to characterise precisely the thermal decomposition process of the studied anionomers, which have two clearly outlined exothermic stages. Hence, additional temperatures were listed in Table 1 for both of the degradation stages at which the heat was released at the highest rate, i.e. the values $T_{DTA_{1\max}}$ and $T_{DTA_{2\max}}$. The relative mass loss at stage 1, which takes place within $T_{DTA_{1\max}}$ =310–360 °C, amounts from 30% for the relatively most stable anionomer no. 2 up to 68% for anionomer no. 1. That mass loss most probably results from decomposition of less stable ether structures of rigid segments and from partial decomposition of urethane structures created, for example, with the participation of less reactive –NCO groups of diisocyanates used in the synthesis process. Exactly within that temperature range, the minimum value of the DTG peak is located, which represents the highest rate of mass loss from samples. At stage 2, on the other hand, which is characterised by the value of $T_{DTA_{2\max}}$ =527–588 °C, the analysed anionomers undergo complete decomposition at practice, so that $\Delta m/m_o$=97–100%. The comparative analysis of the obtained data (Table 1 and Fig. 3) shows that anionomer no. 2 is the most stable material. It was synthesised from aromatic symmetrical diisocyanate MDI and its decomposition at stage 2 ($T_{DTA_{2\max}}$ =541 °C) reached 88%. So, the final degradation took place at that stage which covered even the most stable aromatic structures.

## Conclusions

The analysis of SAXS results shows that the supermolecular structures of the investigated anionomers have a small yet clearly observable degree of phase ordering

**Table 1** Findings from thermal and thermogravimetric analyses of synthesised polyurethane anionomers

| Sample number | Type of diisocyanate | DSC Metler Toledo STAR System | | | Netzsch DSC 200 | | | $T_{DTG_{\min}}$ (°C) | $T_{DTA_{1\max}}$ (°C) | $T_{DTA_{2\max}}$ (°C) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Sample weight (mg) | $T_{g1}$ (°C) | $T_{g2}$ (°C) | Sample weight (mg) | $T_{g1}$ (°C) | $T_{g2}$ (°C) | $\frac{\Delta m}{m_0}.100\%$ | | |
| 1 | TDI | 18.13 | −68 | −12 | Not tested | | | 344 | 350 | 588 |
| | | | | | | | | 66 | 68 | 98 |
| 2 | MDI | 20.92 | −69 | 27 | 7.30 | −68 | 10 | 326 | 313 | 541 |
| | | | | | | | 63 | 40 | 30 | 88 |
| 3 | HMDI | 12.43 | −61 | 72 | 7.10 | −30 | 50 | 346 | 360 | 529 |
| | | | | | | | | 53 | 62 | 97 |
| 4 | IPDI | 16.52 | −62 | 13 | Not tested | | | 356 | 349 | 527 |
| | | | | | | | | 55 | 50 | 100 |
| 5 | HDI | 18.37 | −68 | −26 | Not tested | | | Not tested | | |

which is undoubtedly visible for the anionomers obtained by using the cycloaromatic diisocyanate HMDI, IPDI and aliphatic HDI. On the other hand, the structure ordering of aromatic anionomers turned out much inferior although their polarity was relatively high—as found in [1]. In the investigated samples, the separation of the phases is not so distinct as that which took place, for example, in amphilic polyurethanes produced from HDI and polyoxyethene glycol [6]. So, it is probably the symmetric structure of aromatic diisocyanates and polarity of urethane and urea groups that strongly influences the capability of crystallisation in case of the polyurethane elastomers. In case of polyurethane anionomers (Fig. 5), these factors play less significant roles in the formation of the orderly organised phase, while different spatial effects and strong ionic interactions between the functional groups with electric charges can become decisive [7].

The investigation of phase transitions by the DSC method revealed essential differences within low- and high-temperature changes resulting from glass transition of flexible polyether segments and rigid segments with more diversified urethane and urea structures. It is most probably for that reason that much more complex DSC profiles were recorded for the tested samples at the high-temperature regime. If interactions are within the polyurethane rigid phase, the conclusions drawn from the SAXS and DSC analyses can be found coherent. However, those strong interactions, which increase the rigid behaviour of anionomer macromolecules and the surface energy of the coatings obtained therefrom, can be disadvantageous for some potential applications of synthesised anionomers. One of such applications can be, e.g., binders for ceramic powders. In that case, not only good strength of the $Al_2O_3$–

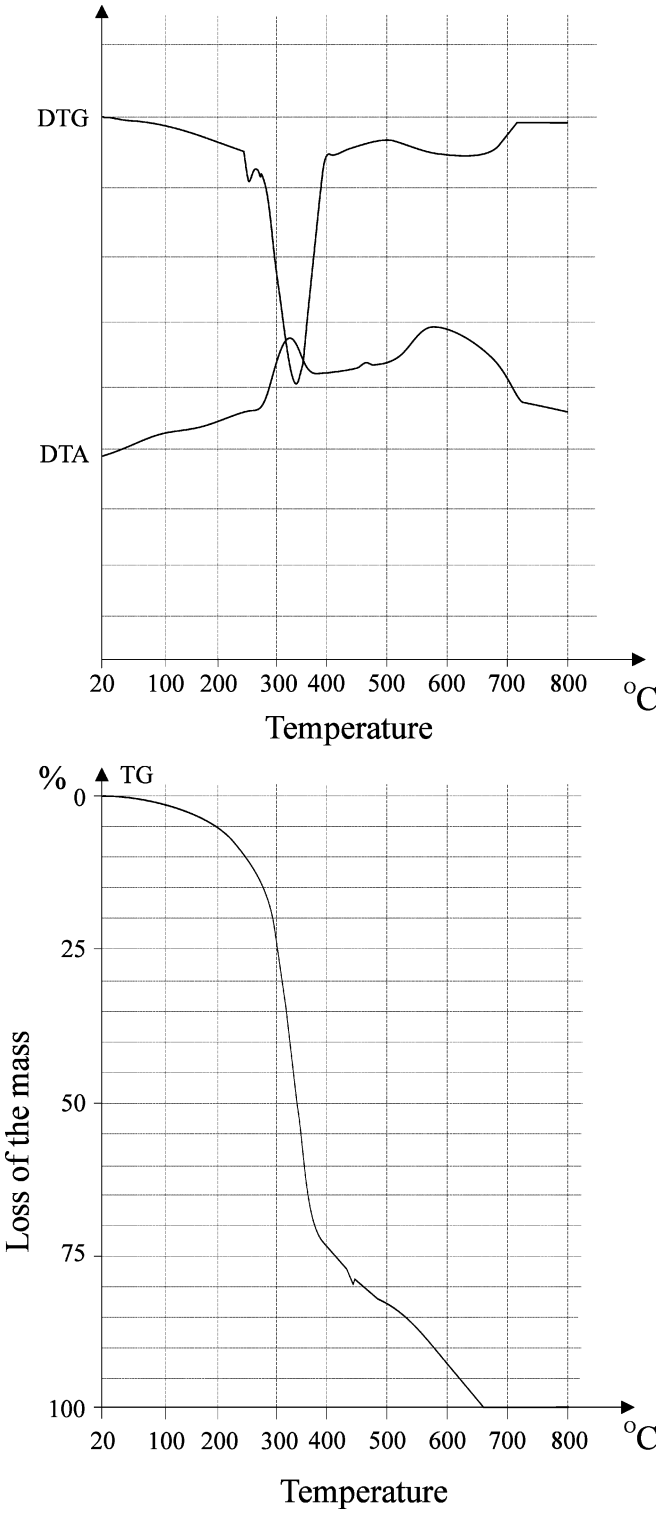


**Fig. 4** TG, DTG and DTA thermograms for polyurethane anionomer no. 1

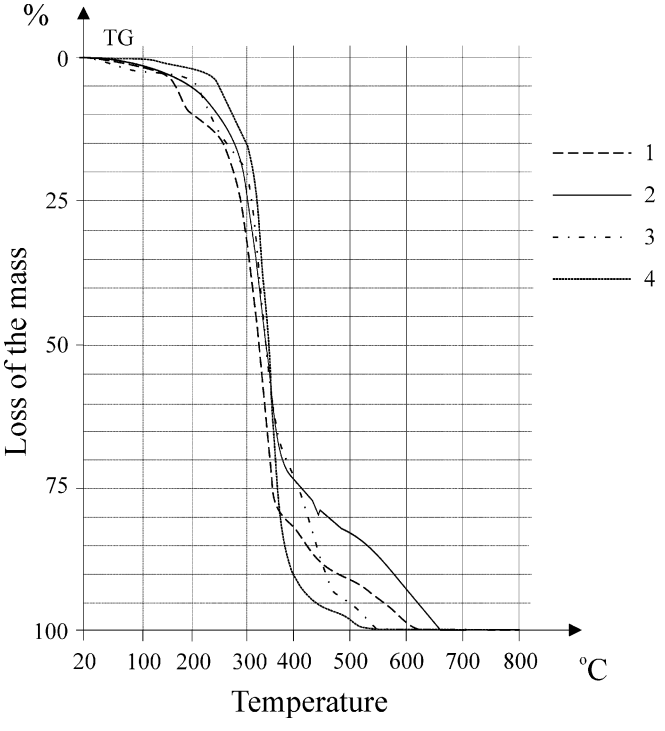


**Fig. 5** TG thermograms for polyurethane anionomers nos. 1–4

polyurethane interphase is required but good adhesion to the ceramic material is also needed. Only under that condition can one expect that the ceramic items moulded in the so-called green state can be subjected to machining before their final firing [8, 9]. Hence, 'cooperation' is required between the reversible glass transition processes in both of the identified temperature ranges.

In accordance with our expectations, the structures of aromatic anionomer nos. 1 and 2 turned out much more thermally stable, while the structure of anionomer no. 3 was more stable within the studied two alicyclic polymers. We failed to take the TG measurements for the relatively poorly stable and flexible anionomer no. 5, which was synthesised from HDI; it was hard to produce a satisfactory big sample, with the weight of about 100 mg, which was necessary for the analysis with the use of the derivatograph F. Paulik, J. Paulik, L. Erdey. The general thermal stability of the synthesised anionomers corresponds to their polarity specifications as found by infrared and DSC methods [1]. It is essential for the considered production process of binders for powdered $Al_2O_3$ that the thermal decomposition process should proceed as uniformly as possible during the firing operation and that performance is much better presented in the TG thermograms of anionomer nos. 1 and 2.

Having in mind the above conclusions, it is advisable to investigate whether any correlation exists between the different polarity specifications as found for the anionomer structures, the observed orderly arrangement of molecular and supermolecular structures and the electrical properties of the coatings obtained from the synthesised anionomers. The electrical properties of those materials can turn out essential for their outlets as environmentally friendly lacquers to be applied by electrostatic spraying on a conductive subgrade. That problem will be the subject for analysis in part 3 of the study.

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