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ORIGINAL CONTRIBUTION

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Polyurethane anionomers synthesised with aromatic, aliphatic or cycloaliphatic diisocyanates, polyoxyethylene glycol and 2,2-bis-(hydroxymethyl)propionic acid. Part 3. Electrical properties of polyurethane coatings

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Abstract The following electrical properties were found for polymer coatings obtained from polyurethane anionomers synthesised with the use of various diisocyanates: volume resistivity, permittivity and dielectric dissipation factor. The effects were discussed from the molecular structures and phase structures of those anionomers on the value of their ionic conductivity and polarizability. The anionomer prepared from the aliphatic diisocyanate was found to offer ionic conductivity; hence, that material can be considered to be a solid electrolyte, which exhibits a considerable susceptibility to structural modifications in the alternating electric field.

Keywords Polyurethane anionomers · Polarity of bonds · Ionic conductivity · Dielectric permittivity

Introduction

More and more attention is paid recently to the synthesis of ionomers, in which the structure makes the controlling factor for the electrical properties, so that those products are not considered typical polymeric dielectric materials but rather the materials which are electrically conducting to some extent. That situation is in particular applicable to polyurethane plastics synthesised in the reaction of diisocyanates, polyols as well as numerous amine-type modifiers and chain extenders. So, for example, considerable polarity and increased ionic conductivity in polyurethane anionomers create the possibility of obtaining new materials with nonlinear properties, applicable in electronics and optics [1–3]. Irrespective of that, the measurements of electrical properties and in particular of dielectric permittivity and ionic conductivity can be utilised to study chemical structures and the arrangement of supermolecular structures in urethane polymers [4]. Moreover, polyurethane ionomers are important from the point of view of their application. Ionomeric light-coloured emulsions and dispersions have long been known to be applicable in environmentally friendly lacquers [5]. The presence of ionic structures, derived from selected types of polyols and tertiary amines which have been additionally incorporated into the polymer chains, modifies further the physical–mechanical properties and surface properties of the items produced of polyurethane plastics [6]. Those structures also affect the interactions resulting from the presence of hydrogen bonds formed with the participation of polar urethane groups, which improves the mechanical properties and thermal stability of the polymer [7]. Moreover, the polyurethane ionomer additives improve the thermodynamic miscibility of polymer blends wherein polar polymers, polyolefins and polystyrene are used, which is essential for easier processing of those materials by means of injection moulding [8].

Having in mind the above questions and the need to search for new electrically conducting coating materials, e.g. as electrolytes for lithium batteries [9], we found it advisable to obtain polyurethane anionomers with the use of aromatic, alicyclic and aliphatic diisocyanates, commonly applicable in polyurethane manufacturing processes, and to study the impact of their chemical and supermolecular structures on the observable electrical properties. The analysis of those properties has to be

preceded by the structural studies of the synthesised anionomers, which were described in part 1 and part 2 of this report [10] (Król et al., manuscript under preparation). The measured electrical properties were presented in this work and the structural implications related to them were discussed

Experimental

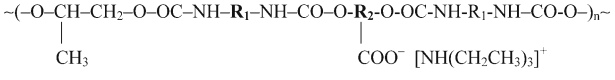
Materials

Polyurethane anionomers [10]:

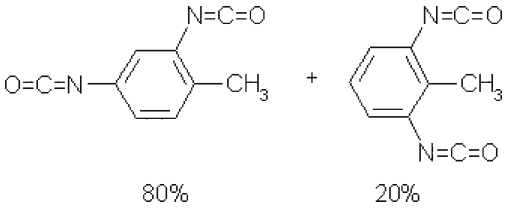
- PU anionomer obtained from the reaction of 2,4- and 2,6-tolylene diisocyanate (2,4- and 2,6-TDI), polyoxypropylene glycol (M_n=450 g/mol) (Rokopol 7p) (M_n=450) and 2,2-bis(hydroxymethyl)propionic acid (DMPA), neutralised with triethylamine (TEA) and extended by means of 1,6-hexamethylenediamine (HMDA); 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)

In obtaining the polymer coatings to analyse their electrical properties, the obtained dispersions were put with an applicator, used to put the painting coatings, on the surface of 9×9 cm pieces of steel sheet which had been previously cleaned and degreased. The coating was formed by conservative water evaporation from the spread anionomer dispersion in the drier at 110°C over about 1 h. The samples were then transferred to the exsiccator where they were cooled to the room temperature. The proper seasoning was continued in an air temperature of approx. 20 °C during the next 10 days. After this time, the coatings were air-dry, i.e. they did not contain any surface-adsorbed water in bigger quantity than it may result from the equilibrium air moisture in the temperature of 20 °C. Just after the measurement, the coating was additionally wiped with acetone.

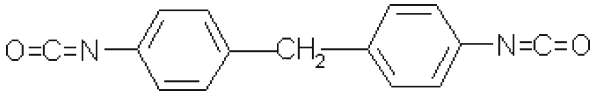
The chain structure of the synthesised anionomers can be presented as follows:



where: $\mathbf{R_1}$—group derived from diisocyanates employed:



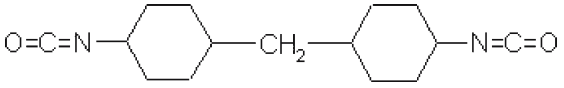
- 2,4- and 2,6-Tolylene diisocyanate (used for the synthesis of sample no. 1)



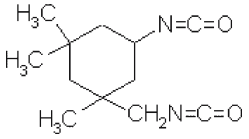
- 4,4′-Methylenebis(phenyl isocyanate) (sample no. 2)

$$O = C = N - (CH_2)_6 - N = C = O$$

- 1,6-Diisocyanatehexane

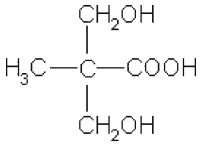


- 4,4′-Methylenebis(cyclohexyl isocyanate) (sample no. 3)



- Isophorone diisocyanate [5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane] (sample no. 4)

$\mathbf{R_2}$—ionic structure derived from bis(hydroxymethyl)propionic acid



Method for determination of electrical properties

Measurements of electrical properties were taken at ambient temperature T=20 °C with the use of a steel

electrode with a diameter of 71 mm. The following properties of the produced coatings were determined:

Volume resistivity (Ω mm)

$$\rho_V = \frac{U \cdot S}{I \cdot d} \tag{6}$$

where U is the value of DC voltage, I is the steady value of current flowing through a sample, S is the surface of electrode, d is the sample thickness, which was then re-calculated into specific conductivity (S/cm^{-1}).

$$\gamma = \frac{1}{\rho} \tag{7}$$

The real part of complex relative permittivity:

$$\varepsilon = \frac{C_x}{C_0} \tag{8}$$

where C_x is the capacitance as measured, and C_0 is the electrode capacity arranged in air, calculated from the formula:

$$C_0 = \varepsilon_0 \frac{S}{d} \tag{9}$$

where ε_0 is the permittivity of vacuum, which amounts to $8.854 \cdot 10^{-12}$ F/m.

Dielectric dissipation factor tanδ

Imaginary part of complex relative permittivity:

$$\varepsilon'' = \varepsilon' \cdot tan\delta \tag{10}$$

The used techniques of covering the steel sheets did not give the opportunity, as the thickness measurements of the obtained coatings made after their final seasoning showed, to get the perfectly even surface required to the electrical measurements. The differences in the coating thicknesses resulted in the fact that the electrode could not adhere to it precisely, which consequently resulted in air gaps at certain locations and the size of that gap reaching one third of coating thickness maximum. (Vacuum application of silver electrodes was not advisable as that could damage the air micro-bubbles present in the coating layer.) Because of that reason, our findings for volume resistivity of the analysed samples have the burden of errors in the order of tens of percentages, which means that in practice only their order of magnitude can be evaluated properly; however, it is quite reasonable to compare them reciprocally.

The shapes of permittivity curves and dielectric dissipation factor curves, on the other hand, can be declared close to their real profiles, although the values for permittivity, if close to 1, are most probably affected by the presence of air bubbles (for air ε=1) in the coating and by the air gap between the electrode and the polymer surface. Table 1 provides the measured maximum and minimum values for the sample thickness and the sample capacitance C_0:

$$C_0 = \frac{\varepsilon_0 \cdot S}{d} \tag{11}$$

where ε_0=8.854·10^{-12} F/m is the permittivity of vacuum; S is the surface of electrode and d is the maximum thickness of coatings which is determined by the sample thickness and size of electrode. The volume current intensity (I) and the volume resistivity have been specified in the table. Resistivity was measured at a voltage of 10 V. The maximum values were taken for calculations as the electrode was touching the coating at the places with the highest thickness.

The parameters for permittivity (designated as ε', the real part, and ε'', the imaginary part) and the dielectric dissipation factor (tg δ) were found from the measurements taken at the sinusoidal voltage with a maximum value of 10 V, within the frequency range from 20 Hz to 1 MHz.

Results and discussion

Interpretation of electrical properties of synthesised polyurethane anionomers

The structural criteria adopted on the basis of structural investigations by infrared and ^{1}H NMR methods made it possible to arrange the obtained polyurethane anionomers in the sequence as below from the viewpoint of their increasing polarity, depending on the type of diisocyanate employed for their synthesis [10]:

$$\begin{aligned} &Anionomer\,5\,(HDI) > Anionomer\,2\,(MDI) > \\ &Anionomer\,1\,(TDI) >> Anionomer\,3\,(HMDI) > \\ &Anionomer\,4\,(IPDI) \end{aligned} \tag{12}$$

The supplementary information on the nature of physical interactions which are decisive for the polarisation phenomena taking place in the studied polyurethane anionomers and which add to the analysed structural parameters can be obtained on the basis of electrical properties investigated in our present study. The most typical in this regard is the value of the real part of complex permittivity ε'. As results from the charts presented in

Table 1 Electrical properties of synthesised anionomers

Sample no.	Type of diisocyanate	Max. thickness of coating (mm)	Min. thickness of coating (mm)	Capacitance C_0 (C)	I (A)	Volume resistivity (Ω mm)	Specific conductivity (Ω^{-1} cm^{-1})	ε' (1,000 Hz)	ε'' (1,000 Hz)	tan δ (1,000 Hz)
1	TDI	0.34	0.12	$1.03 \cdot 10^{-10}$	$3.00 \cdot 10^{-9}$	$4.0 \cdot 10^{13}$	$2.5 \cdot 10^{-13}$	2.66	0.19	0.07
2	MDI	0.43	0.30	$8.15 \cdot 10^{-11}$	$8.50 \cdot 10^{-10}$	$1.0 \cdot 10^{14}$	$1.0 \cdot 10^{-13}$	1.19	0.07	0.06
3	HMDI	0.30	0.12	$1.17 \cdot 10^{-10}$	$1.00 \cdot 10^{-7}$	$1.0 \cdot 10^{12}$	$1.0 \cdot 10^{-11}$	2.57	0.44	0.17
4	IPDI	0.43	0.25	$8.15 \cdot 10^{-11}$	$1.00 \cdot 10^{-7}$	$9.0 \cdot 10^{12}$	$1.0 \cdot 10^{-12}$	1.60	0.10	0.06
5	HDI	0.34	–	$1.03 \cdot 10^{-10}$	$8.00 \cdot 10^{-6}$	$1.0 \cdot 10^{10}$	$1.0 \cdot 10^{-9}$	10.50	4.84	0.46

Fig. 1, the values of ε' for synthesised PU anionomers, as measured within the frequency range 20 Hz–1 MHz, change very little, although the biggest changes were observed for anionomer no. 5 within 20-5. The chain structure for that polymer was in our earlier studies [10] found – in accordance with the adopted structural criteria – to be the most polar one. The much bigger decline in ε' observed for that polymer speaks for the limited capacity of dipoles in that anionomer to follow the orientation of the fast-oscillating electric field. That should be accounted for by the superior deformability of the aliphatic structure in the electric field. When the frequency of oscillating field increases, the dipoles fail to keep pace with those changes, which consequently is responsible for the drop of ε'. The ε' values for other anionomers are clearly lower; they equal to a few units only, and they vary insignificantly only in the specified scope of frequencies. Except for the much lower value of anionomer no. 2 (synthesised with the use of the aromatic diisocyanate MDI) – probably because of the errors resulting from numerous air bubbles in the coating – the values of ε' for other anionomers correspond to the established sequence (12) which is defined by the polarity of their chemical structures. Except for sample no. 5, the profiles of the obtained dispersion curves for ε' should be considered typical for polar polymers. For example, in poly (urethane-imides) modified with diphenylsilanediol, the values of ε' amounted from 3.9 to 3.1 at the frequency of 1.4 kHz [7]. In case of aromatic polyurethanes having the structures of poly(urethane-isocyanurate) inter-penetrating networks (IPN), the values of ε' fell within 4 to 8 for the frequency range of 10^{-1}–10^{6} Hz, depending on the content of the polyurethane component in the composition (0–

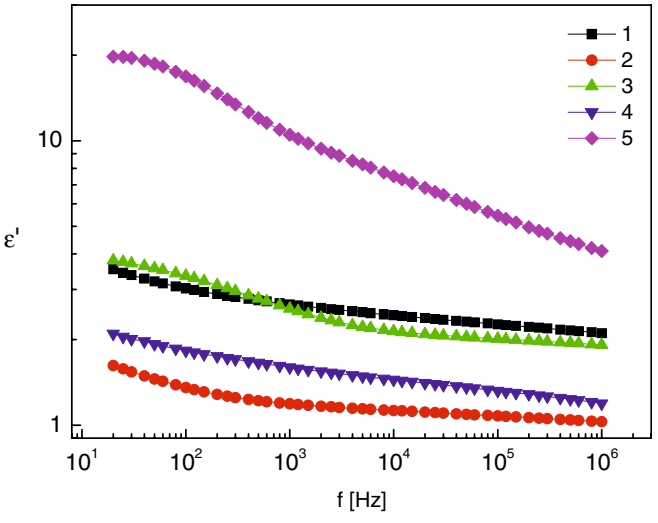


Fig. 1 Relation between real part of electrical permittivity ε' and frequency. *1*, anionomer synthesised from TDI; *2*, anionomer synthesised from MDI; *3*, anionomer synthesised from HMDI; *4*, anionomer synthesised from IPDI; *5*, anionomer synthesised from HDI

100%). Those values were similarly dependent on the frequency to a slight extent only [11].

To compare the effect of the urethane structure type on ε', those values were specified in Table 1 for the frequency of 1,000 Hz. The electrical properties can also be affected by the nature of phase arrangement in the studied anionomers, adding to the effect of chemical structures. As results from the studies described in part 2 of this paper (Król et al., manuscript under preparation), the supermolecular structures of synthesised anionomers show some phase order, which is clearly seen in the small-angle X-ray scattering dissipation curves. That, in particular, refers to ionomers obtained from cycloaliphatic diisocyanates HMDI, IPDI and aliphatic HDI. The structural order in aromatic anionomers obtained from TDI and MDI turned out surprisingly to be much inferior, despite their relatively high polarity found in [10]. It is that factor which, adding to polarity and aromatic nature of the chemical structures, can also affect the specific conductivity observed for the investigated anionomers. In case of polar crystalline polymers, like polyacrylonitrile and polyamide 6,6, the electrical permittivity amounts to 3.5 and 4.0, respectively, while their specific conductivity is in the order of 10^{-15} Ω^{-1} cm^{-1} [12, 13]. As can be observed in Table 1, the values of volume resistivity measured for the tested samples differ very much from each other, even within four orders of magnitude. The values of specific conductivity are consequently in the order of 10^{-13} Ω^{-1} cm^{-1} for aromatic anionomer coatings no. 1 and 2, in the order of 10^{-11} and 10^{-12} for cycloaliphatic anionomers no. 3 and 4, and much more, in the order of 10^{-9}, for aliphatic anionomer no. 5. Much higher conductivity of the synthesised anionomers, even in relation to polar polymers like the mentioned polyacrylonitrile, results from the mobility of COO^- anions and positive counter-ions created by protoned incorporation of TEA to those structures. That accounts for a considerable share of the ionic conductance in polyurethane anionomers. That is confirmed by the findings presented in [5], according to which introduction to the isocyanate prepolymer, produced from IPDI and polyethylene glycol, ionic groups derived from DMPA, yielded the water-soluble polyurethane gels with conductance at the temperature range 0–50 °C increasing from 10^{-6} to 10^{-5} Ω^{-1} cm^{-1}.

The interesting conclusions result, on the other hand, from the measurements of the dielectric loss factor (Fig. 2.). The lowest values of tan δ=0.06–0.07 at 1,000 Hz were obtained for anionomers no. 1, 2 and 4, a fact which suggests that neither aromatic components in the structure nor its polarity contribute much to that phenomenon; but it is rather the scope of conductivity resulting from the chemical structure and supermolecular structure of anionomers which is important. The dielectric loss factor for anionomers obtained with the use of HMDI and HDI is much higher and it amounts to 0.17 and 0.46, respectively, which results from the high conductivity of those materials. The polarizability of their structures, on the other hand, is decisive for increased real part of the complex electrical permittivity.

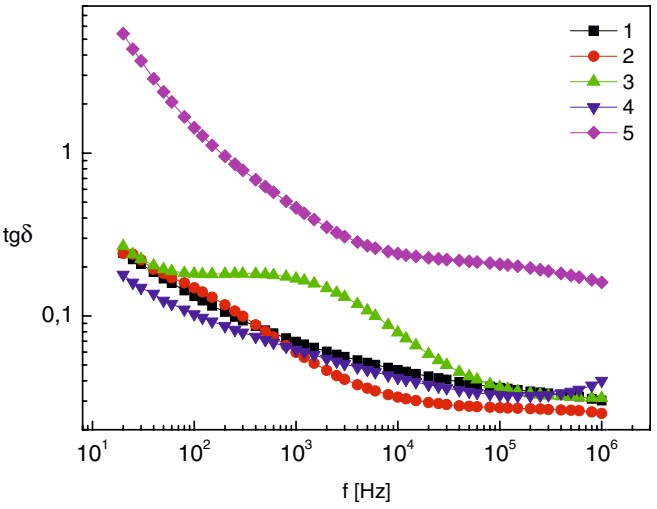


Fig. 2 Relation between dielectric loss factor and frequency. The designations for curves are the same as in Fig. 1

The values of tg δ define the ability of the polymer material to convert the electric energy into thermal energy and they also decline at higher frequencies. For the measurements taken at 20 °C, a poorly distinguished relaxation peak can be observed for every sample at the frequency range of f=1,000–5,000 Hz, which represents the so-called α-relaxation connected with the glass transition of the rigid urethane–urea segments at the temperature T_{g2} (Fig. 3). As we have discussed in part 2 of this paper (Król et al., manuscript under preparation), complex phase transitions can be observed at the temperatures above 0 °C which are connected with the glass transition of the rigid urethane segments and which are responsible for the considerable broadening of the range of T_{g2} [6]. The peak

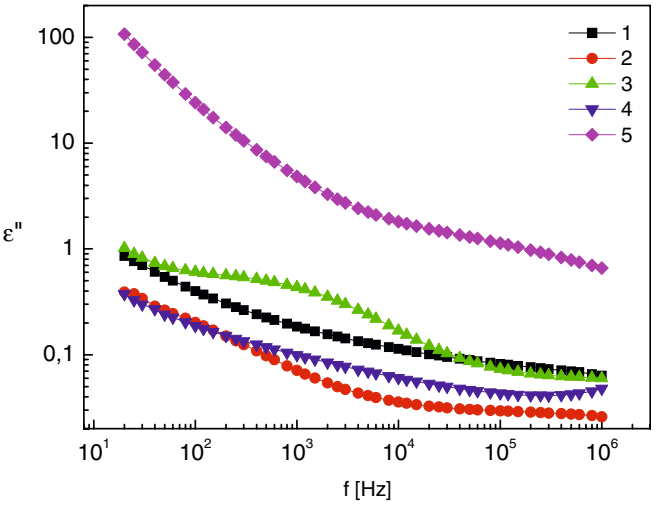


Fig. 3 Relation between imaginary part of electrical permittivity ε'' and frequency. The designations for curves are the same as in Fig. 1

which represents the α-relaxation can be pretty clearly seen in the dispersion curve for anionomer no. 3, synthesised from HMDI, for which the DSC thermogram also shows clearly a single-phase transition at T_{g2}≈50 °C.

The effect of β-relaxation type Johari–Goldstein [14], which is always present in DSC thermograms of all synthesised anionomers within −70 to −60 °C (Król et al., manuscript under preparation) and which is connected with the movements within soft ether-type segments, cannot be found in the recorded curves for dispersion ε″. The probable reason is that it can be possibly observed at 20 °C for much higher frequencies only. For example, in case of segmented PU ionomer synthesised from MDI and poly-oxyethylene glycol, the peak for β-relaxation in the dispersion curve ε″ could be observed at 20 °C not earlier but above 10^8 Hz [11].

Figures 4 and 5 present the charts for the relation ε″=*f*(ε′) which refer to anionomers 5 and 1– 4, respectively. These are the totals for the relations resulting from the Debye relaxation model and for the strongly outlined ionic conductivity. The conductivity is clearly dominant in the samples 1, 2, 4 and 5. Hence, the typical Cole–Cole semicircles or those deformed after incorporation of the correction factors to the Debye equation [15] are not visible in practice, except for the diagram for sample no. 3, in which the additional semicircle and the conductivity curve were demonstratively plotted (Fig. 5.). The actual profiles for the Cole–Cole diagrams ε″=*f*(ε′) make the total for both of the dispersion curves. (The chart for sample no. 5 – Fig. 4 – was subjected to re-scaling because of the units applicable to the ε″ axis.) So, both the polarisation effects and ionic conductivity can be observed in every sample. However, conductivity is dominant in most cases and it is hard for that reason to analyse the polarisation phenomena in the synthesised anionomers. The information on that subject must hence be derived from the reports on the

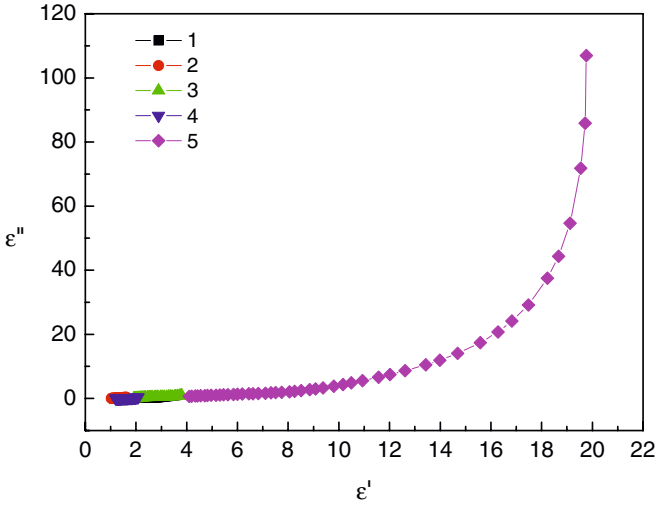


Fig. 4 Cole–Cole diagram for anionomer no. 5

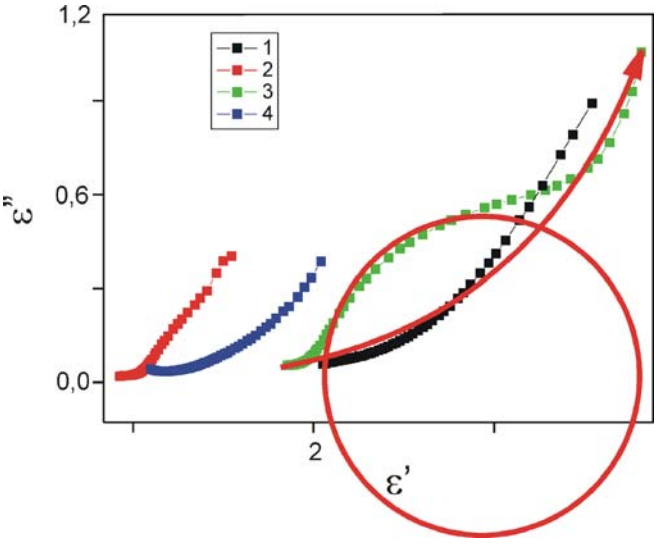


Fig. 5 Cole–Cole diagrams for anionomers no. 1–4. The designations for curves are the same as in Fig. 1

analysis of Cole–Cole diagrams for classical polyurethanes, i.e. typical dielectric materials [16].

Conclusions

The investigations made on electrical properties supplement the knowledge on the structures of obtained anionomers which comes from the earlier structural studies [10] (Król et al., manuscript under preparation). The polymer coatings formed by application of the synthesised polyurethane anionomers on the subgrade feature the specific conductivity within 10^{-13}–10^{-9} Ω^{-1} cm^{-1}, depending on the type of diisocyanate used. The aliphatic structure of diisocyanate HDI yields the coating material with higher conductivity and improved polarizability in the alternating electric field, which results in higher polydispersity of electric permittivity and dielectric loss factor. The aromatic structure of anionomers produced of diisocyanates TDI and MDI offers the unexpectedly inferior electric conductivity. The interesting electrical performance – considerable conductivity at the level of 10^{-11} Ω^{-1} cm^{-1}, structural polarizability and presence of phase transition connected with the phenomenon of α-relaxation of rigid urethane–urea segments – was observed for anionomer no. 3 derived from the cycloaliphatic diisocyanate HMDI. The analysis of Cole–Cole diagrams proved that both polarisation effects and ionic conductivity could be found in the studied anionomers. Those features result from the structure of polymer chains, from the presence of ionic structures and from the arrangement within the supermolecular structures as well, which is jointly decisive for the electrical properties of the investigated materials.

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