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Morphology, Dielectric Relaxation and Conductivity of the Novel Polyurethane Ionomers Based on Poly(Thetramethylene Oxide)

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The thermal transitions, microphase structure, local segmental and conductivity relaxation of the novel polyurethanes (PUs) based on the poly(tetramethylene glycol) as soft segments (SSs) and 4,4'-diphenylmethane diisocyanate-1,4-butane diol sequences of various length as hard segments (HSs) containing ionic groups in SSs are studied by calorimetry, X-ray scattering and dielectric relaxation spectroscopy.

Keywords: Polyurethane ionomers; morphology; ionic conductivity

INTRODUCTION

Segmented polyurethanes (PUs), among others features, are known as matrices for solid polymer electrolytes (SPEs) [1-3]. Those may be either systems that consists of polymer mixed with a salt [1] or the PUs bearing a salt groups [2,3]. It have been recently synthesized by us the novel polyurethanes containing ionic groups in the polyether soft segments (SSs). that characterized by two-phase morphology and either single-ion or proton conductivity mechanism [4,5].

Here we report new result on the thermal, structural and conductivity properties of the different hard segment (HS) length PUs

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based on poly(tetramethylene oxide) SS bearing metal-carboxylate groups.

EXPERIMENTAL

The PUs were synthesized using poly(tetramethylene glycol) (PTMG) (mol.wt.1040, Merck Chemical Co.), 1,4-butanediol (BD) (99%,Aldrich Chemical Co.), 4,4'-diphenylmethane diisocyanate (MDI) and pyromellitic anhydride (PMA) (Aldrich Chemical Co.) as starting materials and dimethyl formamide (DMF) (Aldrich Chemical Co.) as a solvent.

Carboxyl-containing oligoether (I) (SS precursor) ended by OH-groups was prepared using PTMG and PMA in the ratio 2:1. A series of isocyanate compounds (II) (HS precursors) ended with NCO-groups were synthesized using MDI and BD in the ration 1:0, 2:1, 3:2, 4:3 and 6:5 and coded as B0, B1, B2, B3, B5, respectively. The acid form PUs containing B0, B1, B2, B3, and B5 HSs were synthesized by the reaction of (I) with (II) with NCO/OH=1 and coded as M1B0H, M1B1H, M1B2H, M1B3H, and M1B5H, respectively. The ion-containing PUs were prepared by treating of the corresponding acid-containing PUs with NaOH and coded as M1B0Na, M1B1Na, M1B2Na, M1B3Na, and M1B5Na, respectively.

The general molecular structure of the PUs prepared is shown in Figure 1.

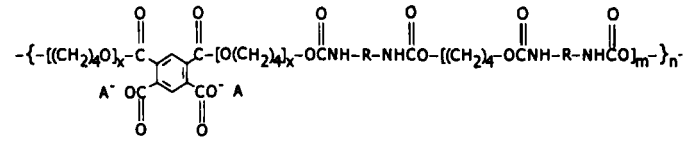

FIGURE 1 General molecular structure of the polyurethanes under study, R is 4,4'-$C_6H_4CH_2C_6H_4$; x is 14; m is 0, 1, 2, 3 or 5; A is Na^+ , n is a polymerization degree.

DSC curves were recorded by Perkin-Elmer type differential scanning calorimeter (DSM-2M) using a heating rate of 16 K/min under a He purge. SAXS experiments were conducted using Kratky slit-

collimated camera (copper anode emission). The FFSAXS-3 program[6] was using to calculate the microphase structure parameters. DRS isothermal measurements, in the frequency range 10^{-1} – 10^{6} Hz and the temperature range 0 – 100°C were carried out using a frequency response analyzer (Schlumberger SI 1260). The samples for all the experiments were obtained from spin-cast films.

RESULTS AND DISCUSSION

The values of glass transition temperature, T_g, heat capacity jumps in a low temperature region, ΔC_p together with the weight fraction of SSs, and the T_g values calculated for the PUs using Fox's equation, with the supposition of a one-phase state of the system, and termed as $T_{g,F}$ are presented in Table I.

TABLE I Calorimetric data of the PU ionomers studied

Polyurethane code	T_g, °C	ΔC_p, J/K	W_1, wt.pt.	$T_{g,F}$, °C
M1B0Na	-67	0.192	0.887	-63
M1B1Na	-59	0.320	0.782	-51
M1B2Na	-55	0.246	0.694	-40.5
M1B3Na	-56	0.188	0.630	-31
M1B5Na	-55	0.108	0.530	-18

As we can see, all polymer materials are completely noncrystallizable at any temperatures. Transition from the M1B0-based polymers to M1B1-based ones leada to decrease of the T_g values.. The increase of a length of HSs is accompanied by initial increasing the ΔC_p values upon transition from M1BONa to M1B1Na with subsequent decreasing of corresponding values for the last members of the series.

The T_g values for the PUs under study by far exceed that of the PTMO which is characterized by the T_g value of about 185 K [7]. Thus, the primary cause of the differing T_g's must be attributed to the MDI and PMA fragments dissolved in the SS matrix. At the same time, one may connects the decrease of T_g of all the PUs upon introduction of the salt groups to transition of the PMA fragments from the SS matrix into ionic aggregates. The low level of T_g (about –40°C) is very important for applications of various polymers as SPE matrix [8]. It is interesting to point out, in this connection, that the T_g values for all the

PUs studied do not exceed −55°C that is good enough for SPE applications. The data of Table I demonstrate that the T_g values of all the PUs, beginning with M1B2 series, are below $T_{g,F}$ values calculated in approach of one-phase system. So these samples are effectively microphase-separated.

SAXS curves of the M1B0Na, M1B1Na, M1B2Na, M1B3Na, and M1B5Na samples are shown in Figure 2. They are very closed to each other in the low angle region of theirs. However, what about the region of the more values of the scattering angles (in the q range from 0.75 to 1.25 nm^{-1}) the diffraction curves are different, especially in the case of the M1B0Na, M1B1Na, and M1B2Na samples. The same type diffraction maximum is present in that scattering angle region. Its intensity decreases with increasing a length of the HS segments. The diffraction peak of other type is arisen at the scattering angles from 0.25 to 0.5 nm^{-1}. Its intensity, in contrary to the maximum at the larger scattering angle values, increases along with transition to the PUs of the larger HS segments. The spacing values that correspond the position of the SAXS curve maxima of the PUs at hand are presented in Table II. One can see that the Bragg spacing values of the first diffraction maxima are in the range from 17 to 22 nm and they increase with increasing the HS length. Such maxima are typical for the microphase-separeted structures for other segmented PUs [9]. As against this the Bragg spacing values, that reflect the position of the second diffraction maxima (the ionic peaks), are very closed to each other and are, at an average, of about 7 nm.

It follows from the SAXS patterns that a presence of ionic groups lead to arise the ionic peak on SAXS patterns that is evidence of forming ionic aggregates. In the case of the ionic form PUs, beginning with M1B2 series, the ionic aggregates are formed in the SS microdomains located between the HS lamella-like microdomains.

D.c. conductivity values (σ_{dc}) obtained by an extrapolation of the σ_{ac} low frequency values to the zeroth frequency are presented in Table II We have to point out increase of a length of the HSs leads to decreasing the σ_{dc} values.

As it was shown before the PUs of acid form such as M1B1H develop protonic conductivity as against the corresponding ion-containing analogues that are characterized by cationic conductivity mechanism [4,5]. The data obtained give a possibility to conclude that in both of the cases the polyether-rich microphase serve as a conducting one and a conductance of the materials is realized by a movement of the

proton/cation over the polyether-rich domains joined together to form a continuous percolation structure. The PUs of acid form are more favorable for protonic transport than the corresponding metal-carboxylate analogues for cationic transport.

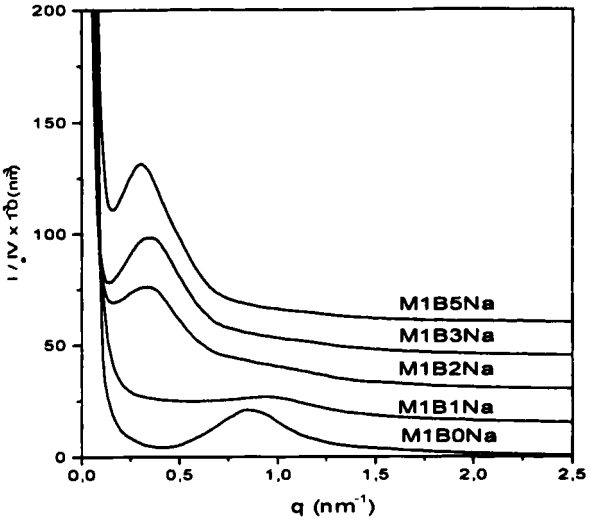

FIGURE 2 Small-angle X-ray scattering curves of the PU ionomers studied..

TABLE II Morphology parameters and d.c. conductivity values of the PU ionomers studied

Polyurethane code	D_{PU} , nm	D_{ion} , nm	σ_{dc} S/cm
M1B0Na	-	7.0	-
M1B1Na	-	6.9	1.1×10^{-8}
M1B2Na	17.3	6.6	2.2×10^{-9}
M1B3Na	18.5	7.1	6.5×10^{-10}
M1B5Na	21.7	7.1	1.5×10^{-10}

CONCLUSIONS

Summarizing, differential scanning calorimetry, wide and small-angle X-ray scattering and dielectric relaxation spectroscopy techniques were used to study glass transition behavior, structure, morphology, conductivity and dielectric relaxation features in a series of polyurethanes that content Na^+ - carboxylate groups in the polyether segments, of a different length of the hard segments. It is shown that increase of a length of the HS leads to microphase separation of the segments of a different nature. As a consequence, the T_g values of the PUs of all HS length do not exceed -55°C. A presence of the ionic groups leads to forming the ionic aggregates. It follows from SAXS data that in the case of the ionic form PUs, beginning with M1B2 series, the ionic aggregates are formed in the SS microdomains located between HS lamella-like microdomains. The d.c. conductivity decrease with increasing the HS length.

Acknowledgment

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