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Properties of urethane elastomers

IV. Depolarization currents from poly(azourethaneurea)

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Summary

The dielectric relaxation processes in poly(azourethaneurea) prepared from diphenylmethane-4,4'-diisocyanate (MDI) and poly(ethylene adipate) glycol were studied in the range 200-390 K using thermally stimulated depolarization currents (TSDC). The TSDC spectra obtained on original sample, annealed sample, and both annealed and stretched sample showed significant differences which were explained in terms of the supramolecular structure of polymers. It was accepted that the polymers have a multiphase supramolecular structure.

Introduction

In previous papers of this series(1-3), the dielectric relaxation processes in polyesters-based polyurethanes were investigated in connection with thermal history and chemical structure, using thermally stimulated depolarization currents (TSDC) and electron microscopy methods. The annealing effects on the dielectric properties were explained in terms of the supramolecular structure of polymers. It was accepted that besides the main hard and soft phases, having ordered and respectively amorphous structures, some other mixed microphases with intermediate structures exist. The structure of each phase is determinated by its hard segment concentration, which increases from the elastic-amorphous phase to the hard-ordered phase.

Using X-Ray and thermal methods, Wilkes and Yusek(4) showed that the supramolecular structure of urethane elastomers is sensitive to the mechanical treatments; stress develops a better order in polymer. The level of the stress-orientation was found dependent both on composition and on the degree of stretch.

The present work analyses the TSDC results on poly(azourethaneurea) in connection with thermal and mechanical treatments.

Experimental

The poly(azourethaneurea) was synthesised from one mole of poly(ethylene adipate)glycol, two moles of diphenylmethane-4,4'-diisocyanate (MDI) and a proper amount of dimethylformamide giving an prepolymer with free $-NH_2$ groups. The macromolecular chains were then extended by formation of $-N{=}N-$ groups upon oxidation in air at room temperature in presence of Cu(I)

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*To whom offprint requests should be sent ions. Detailed aspects on the reaction mechanisms and kinetic data are presented elsewhere (5).

The TSDC measurements were performed on original films, annealed films,stretched films and both stretched and annealed films.

Polymer films about 0.1mm thick were prepared by casting dilute dimethylformamide-polymer solutions on clean glass plates. After removal from the support,the films were washed with water and then dried in vacuum for two hours at 60°C.

The films were stretched uniaxially 200% at room temperature. The annealing of the films was performed at 100°C for one hour in the same chamber used for TSDC measurements. A special sample support was designated in order to draw and to maitain constant the film elongation during the TSDC measurements.

Before TSDC measurements the films were provided with vacuum-evaporated silver electrodes of circular form(ϕ=13mm). Measurements were carried out in dry N_2 at normal pressure using a device described elsewhere (6).

The thermal cycles of polarization and depolarization of samples consisted of the following steps.A sample with a polarization field of 15kV/cm was warmed up to the polarization temperature T_p (75°C for original sample and stretched sample,and 100°C for annealed and stretched sample) which was maintained for a polarization time t_p of 20 min.; after cooling to 200K using liquid N_2, E_p was removed and the sample was short-circuited for 10 min. in order to eliminate the rapid depolarization currents;then the depolarization currents were recorded at a heating rate of 3.5 K/min.

Results and discussion

Figure 1 presents the TSDC thermograms of the original and annealed samples. A comparative analysis of the thermograms reveals that dielectric relaxation spectrum of the original sample underwent changes by annealing. The main observations are the decrease of the α peak intensity and the arrival of an additional α' peak. Also,the β peak slightly increased in intensity and shifted to lower temperatures. A similar temperature shift was observed for α peak too.

The temperature found for β , α and δ relaxation processes are close to those observed for the corresponding processes from polyester-based polyurethanes (3,2). The activation energies were also found in the same value ranges. On the other hand,similar annealing effects were observed for these two types of polyurethanes.

These observations may suggest that the α and δ peaks originate from soft and hard domains respectively: α process involves motions within the amorphous portions of the flexible polyester segments and δ process involves motions within the rigid domains. The β process may be ascribed to the motion of the polyester carbonyl groups.

According to the multiphase structure approach (1-3), shortly presented in the introduction section,the distinct α' peak may be attributed to a new separate microphase generated by annealing; during the annealing process,the hard segments, randomly oriented within the polymer amorphous domains,segregated up to a certain extent which is probably dependent on

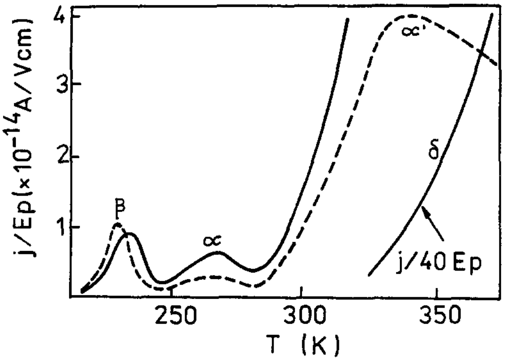

Fig.1. TSDC spectra of poly(azourethaneurea):
——— original film
----- annealed film

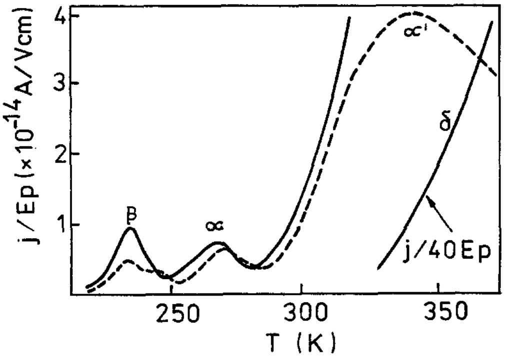

Fig.2. TSDC spectra of poly(azourethaneurea):
——— original film
----- stretched film

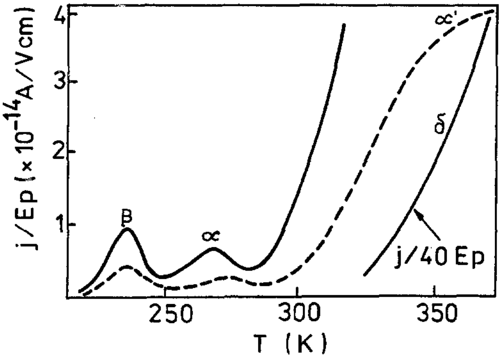

Fig.3. TSDC spectra of poly(azourethaneurea):
——— original film
----- stretched and annealed film

the annealing conditions such as temperature and time of annealing. The annealing conditions dependence of the supramolecular structure of this urethane elastomer is now in progress in our laboratory. The new microphase evidenced by α' peak has a supramolecular structure with an intermediate order degree determined by a specific hard segments concentration situated between those of soft and hard domains.

The TSDC thermogram of the stretched sample also shows significant changes (Fig.2). The most remarkable one is that the singular β peak splits in two peaks of lower intensities. As previously mentioned, the β process in original samples is correlated with the motions of the polyester carbonyl groups.

Threfore, these two separate peaks for drawn samples could be assigned to the carbonyl group motions within the unoriented and stress-oriented polyester domains; higher temperature peak corresponds to the stress-induced domains. The decrease of the β peak intensity may be attributed to the diminution of the carbonyl polarization determinated by internal stress.

The α peak slightly decreased and shifted to higher temperatures (Fig.2); stress hinders the motion of the polyester segments. The additional α' peak is smaller and located at higher temperature comparatively with that observed in annealed sample (Table 1). These observations suggest that the stress-induced order in the mixed phase is less developed than that induced by annealing. This is probably due to the presence of the internal stress in stretched sample.

In Fig.3, the TSDC thermogram of stretched and annealed film is presented comparatively with that of original sample. The thermal treatment of stretched sample enhanced the decrease of the α peak intensity, shifted α' peak to higher temperatures and brought together the β peaks in a singular one. The futher decrease of the α peak intensity and the shift of the α' peak indicate that a better order was developed upon stretching; the extent of the amorphous phase diminished, and the intermediate phase underwent restructuration in a manner which retains considerable orientation of the hard segments.

Table 1. The relaxation characteristics of polyurethanes

Polymer	Peak temperature (K)				Apparent activation energy(eV)			
	β	α	α'	δ	β	α	α'	δ
Original	235	268	-	-	0.61	2.01	-	2.98
Annealed	230	265	337	-	0.58	1.95	2.40	-
Stretched	232;242	269	341	-	0.50;0.65	2.05	2.45	-
Stretched and annealed	233	270	363	-	0.62	2.10	2.57	-

The relaxation characteristics of the samples derived from TSDC spectra are presented in Table 1. The apparent activation energies were determined using the initial current rise method, applied to the cleaned TSDC peaks.

References

1. I.Diaconu, C.Ciobanu and Cr.I.Simionescu, Polym.Bull., 20, 195(1988)
2. I.Diaconu, C.Ciobanu and Cr.I.Simionescu, Polym.Bull., 21, 203(1989)
3. I.Diaconu, C.Ciobanu and Cr.I.Simionescu, Europ.Polym.J., accepted for publication, 1989
4. C.E.Wilkes and C.S.Yusek, J.Macromol.Sci.-Phys., B7(1), 157(1973)
5. C.Ciobanu and I.Diaconu, to be published, 1990
6. I.Diaconu and S.Dumitrescu, Europ.Polym.J., 14, 971(1979)

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