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1965

SovietRxiv

Abstract

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ON THE CRYSTALLIZATION AND GLASS TRANSITION OF POLYETHER-URETHANE BLOCK COPOLYMERS

(Presented by Academician B. A. Arbuzov, January 20, 1965)

Recently there has been a considerable increase in interest in problems of the synthesis and physicochemical investigation of the structure and properties of graft and block copolymers. However, mainly graft copolymers have been studied, whereas the number of similar works on block copolymers is relatively small.

In the present communication we give some observations on the regularities in the change of the glass-transition temperature T_c and on the influence of crystallization processes on it for a number of model urethane block copolymers of the general formula:

$$(-\mathrm{A}-\mathrm{OCONHRNHCOO}-)_{1-n}(-\mathrm{B}-\mathrm{OCONHRNHCOO}-)_{n}, \qquad (1)$$

where A is a block of an aliphatic polyester: polyethylene glycol adipate (PEA) or polydiethylene glycol adipate (PDEA), and B is a block of a polyester based on isomeric bis-(β-hydroxyethoxy)-phenylenes and adipic acid:

$$[-\mathrm{OC_2H_4OC_6H_4OC_2H_4OCOC_4H_8CO}-]_x, \qquad (2)$$

designated below, respectively according to the order of attachment to the benzene ring (para, meta, and ortho), as *n*-PPA, *m*-PPA, and *o*-PPA.

Thus, the objects of study were series of block copolymers based on the following pairs of polyesters: PEA –*n*-PPA, PEA –*m*-PPA, PEA –*o*-PPA, PDEA –*m*-PPA, PDEA –*o*-PPA. For each series of copolymers, n in formula (1) was varied from 1 to 0. The values of T_c were found from thermomechanical curves recorded on an automatic recording apparatus (^{1}) with a constant load (16 kg/cm^2) on the specimen.

It should be noted that the curves of the block copolymers of the series with polyethylene glycol adipate, while having certain individual features associated with the nature of PPA, vary on the whole in an analogous manner from specimen to specimen within each series; this gives us the right to restrict ourselves to considering the thermomechanical curves of one such series. An analogous

Figure 1

Figure 1: Figure 1

regularity is also observed in the changes of the curves of the different series with polydiethylene glycol adipate.

Figure 1 presents the thermomechanical curves of block copolymers of the PDEA —*m*-PPA series. Polydiethylene glycol adipate urethane is a noncrystallizing polymer; on its thermomechanical curve (curve 1) the transition to the highly elastic state is distinctly visible, and—less distinctly—to the viscous-flow state. The other component, *m*-PPA-urethane, is capable of crystallizing, and on the thermomechanical curves of specimens with a predominant content of the corresponding blocks (60 and 80 mol. %, curves 3 and 4), the second transition is associated with the melting of *m*-PPA crystals. This may be judged from the fact that the temperatures of these transitions differ little from the melting temperature of *m*-PPA-urethane.*

The sample with 30 mol.% *m*-PPA, judging from thermomechanical curve 2, is not crystalline. However, the decrease in the growth of deformation in the region of 55-60° is evidently associated with crystallization of the polymer during the experiment. Attention is drawn to the presence of a similar effect on curve 3. However, a more detailed consideration of the phenomena of crystallization and melting in polyester-urethane block copolymers will evidently be the subject of a separate communication.

Fig. 1. Thermomechanical curves of copolymers of the PEA—*m*-PPA series. Constant load 16 kg/cm^2. 1 —0; 2 —30; 3 —60; 4 —80; 5 —100 mol.% *m*-PPA. The arrows indicate the onset of crystallization of the samples during heating.

The glass-transition temperatures determined from the thermomechanical curves under consideration fall well on a straight line connecting the glass-transition temperatures of homopolyurethanes based on PEA and *m*-PPA (Fig. 2, curve 1). Since a linear decrease in T_c of the copolymers is observed as a function of the content of PEA blocks, the latter should apparently be regarded as a kind of plasticizer with respect to the *m*-PPA blocks.

It was essential to determine whether the regularity found is retained on passing to block copolymers in which, along with block B, block A is also capable of crystallizing. The thermomechanical properties of copolymers composed of the above-mentioned *m*-PPA blocks and polyethylene glycol adipate (PEA) blocks were studied. Since the presence of a crystalline phase in a polymer can affect the value of its glass-transition temperature (2), in addition to recording the thermomechanical curves of samples aged over time, curves of the same block copolymers were recorded after their amorphization, which was carried out by

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* These conclusions are in good agreement with X-ray structural and thermographic studies of these specimens.

Fig. 2 and Fig. 3: plots of T_c versus aromatic-block composition

Figure 2: Fig. 2 and Fig. 3: plots of T_c versus aromatic-block composition

heating the samples above the melting temperature of the crystalline phase, followed by quenching in liquid nitrogen. The quenched samples were transferred to the thermomechanical unit block cooled to −50, −60°, after which recording of the thermomechanical curves was begun.

Figure 3 presents the dependence of T_c on composition for the PEA—*m*-PPA series. As can be seen, for the amorphized samples, as in the preceding case, a linear increase in the glass-transition temperature with increasing PPA content is characteristic (curve 1). However, for samples aged over time (up to 6 months), the pattern of behavior is different (curve 2): T_c of copolymers with a predominant PEA content (not less than 60 mol.%) becomes equal to T_c of PEA-urethane, whereas for copolymers in which the PEA content is below 60%, T_c remains equal to the glass-transition temperature of the amorphized samples or slightly below it.

The following explanation of the observed facts seems probable to us. For copolymers in which block A is in the amorphous state (is not capable of crystallizing or is amorphized), a continuous decrease in the glass-transition temperature from the values of T_c of B-urethane to T_c of A-urethane is characteristic, since the latter is a plasticizing agent with respect to the arylene-containing blocks B. Obviously, in such a case, since plasticization occurs at the molecular level, T_c should decrease linearly as a function of the percentage content of the aliphatic block A. In the case of samples in which the A-block crystallizes, prolonged storage under room-temperature conditions leads to the appearance in the copolymers studied of crystalline formations as a result of

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Fig. 4. Microphotographs in polarized light of spherulitic formations in copolymers of the PDÉA-o-PPDA series. 100×. **a**–0; **b**–30; **v**–50; **g**–70 mol.% PDÉA. The specimens crystallized for 3 hours at room temperature.

crystallization of each of the types of blocks. The latter circumstance must inevitably lead to the appearance of microheterogeneity in the samples, just as was noted for graft and block copolymers composed of polar and nonpolar components (3,4). Microregions in which blocks of one nature are grouped must evidently exhibit a number of properties inherent in that component in the form of a homopolymer and, in particular, have its glass-transition temperature. Therefore, in copolymers in which the aliphatic block is polyethylene glycol adipate and in which it is no less than 60 mole %, the glass-transition temperature, after prolonged storage, becomes equal to the T_c of PEA-urethane. A completely analogous pattern of change in T_c is observed in the series with para- and ortho-phenylene-containing B blocks (*p*-PPA and *o*-PPA).

Fig. 2

Fig. 3

Fig. 2. Dependence of T_c on the composition of copolymers of the PEA—m-PPA series.
1 —amorphized samples, 2 —stored for 6 months at room temperature

Fig. 3. Dependence of T_c on the composition of copolymers of the PEA—m-PPA series.
1 —amorphized samples, 2 —stored for 6 months at room temperature

In samples in which the content of block B is greater than 40%, T_c is appreciably higher than that for polyethylene glycol adipate urethane. As can be seen from the thermomechanical curves, 40% is the limiting concentration of block B above which the melting effect of the crystallized aliphatic block A is absent on the curves. Consequently, in those cases where separation of the aliphatic block A as an independent crystalline phase does not occur in the samples, their glass-transition temperature is determined by the T_c of the B blocks plasticized by A blocks. This evidently also explains the fact that prolonged storage of samples with polydiethylene glycol adipate does not lead to a change in their glass-transition temperature in comparison with the amorphized samples (Fig. 2, 1 and 2). The decrease in glass-transition temperature in such samples is similar to that observed upon plasticization of crystalline homopolymers with low-molecular-weight compounds ([5]).

For plasticized crystalline polymers it was noted that the size of crystalline formations depends on the amount of plasticizer introduced ([6]). It is of undoubted interest to determine whether the noted regularity is also observed for the series of block copolymers we studied, which, judging by the nature of the change in T_c, may be regarded as systems of arylene-containing blocks chemically plasticized by blocks of an aliphatic polyester. Figure 4 shows microphotographs of spherulitic formations observed in samples with different ratios of PEA and *o*-PPA blocks. The specimens were prepared by applying a thin film of the melt onto a microscope slide, followed by holding for 3 hours at room temperature.

temperature. Observation and photographing of the specimen were carried out with an MIN-8 microscope in crossed polaroids. As can be seen, a fine-crystalline structure is characteristic of *o*-PFA-urethane. In the block copolymers, a successive increase in the size of crystalline formations is observed with increasing content of the PDEA block. All this is in good agreement with the data of works (5) and (6), allowing the introduction of aliphatic blocks into an arylene-containing polymer to be regarded as chemical plasticization of the former by the latter.

Thus, the results of the present work show that crystallization processes in block copolymers affect their vitrification. The glass-transition temperature of amorphous copolymers depends linearly on composition. Crystallization of the component with the lower T_c leads to a decrease in the T_c of the copolymer (over a more or less broad range of compositions) to the value characteristic of the corresponding homopolymer. The component with the lower glass-transition temperature in a block copolymer may be regarded as an internal plasticizer, the introduction of which creates favorable conditions for crystallization of the blocks of the high-melting component.

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Received
12 I 1965

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