THERMAL PROPERTIES OF BLOCK COPOLYMERS POLYAMIDE-6–POLYBUTADIENE

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Polyamide-6-block-polybutadiene copolymers have been prepared by the anionic polymerization of ε-caprolactam in presence of α,ω-dihydroxy terminated polybutadiene. TG, Hi-Res[TM] TGA, DSC, TMDSC and DMA techniques have been applied. The suitability of the methods used to determine the content, thermal stabilities and glass transition temperatures of the components constituting the block copolymer is discussed.

Keywords: block copolymer, glass transition temperature (T_g), melting temperature (T_m), polyamide-6, polybutadiene, thermal stability

Introduction

Polyamide-6-block-polybutadiene copolymers represent a relatively new class of materials, intended for such applications for which the toughness of conventional polyamide-6 (PA 6) is insufficient, especially below the freezing point.

The anionic polymerization of ε-caprolactam (CL), the chains of which start their growth on suitably modified end-groups of telechelic polybutadienes (PBD), is an elegant route to such copolymers [1–3]. Basically, the procedure consists in a transformation of the hydroxy end-groups of the telechelic polybutadienes to the N-acyllactam growth centers, followed by the anionic polymerization of CL, Scheme 1.

In order to functionalize α,ω-dihydroxy terminated polybutadiene (DHPBD), dissolved in the melt of CL, aromatic diisocyanates proved to be useful, especially 2,4- or 2,6-toluene diisocyanate (TDI); thus,
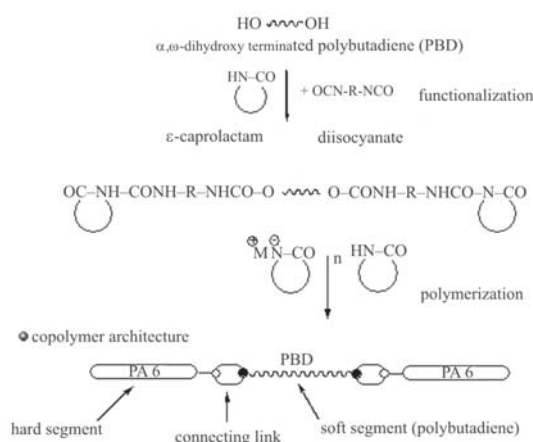
Scheme 1 Preparation of poly(ε-caprolactam)-block-polybutadiene

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N-acyllactam growth centers are formed on PBD [3]. When an initiator is added to the polymerization system containing the telechelic polymer functionalized in this way, the block copolymer is formed within tens of minutes, depending on the polymerization temperature and the concentration of the initiation system.

Ideally, the resulting block copolymer is of the ABA type, individual blocks being connected by links, the structure of which is given by the end groups of the prepolymer and the functionalization agent used.

Mechanical properties of the copolymers thus prepared depend on the content of the elastic phase incorporated and its molar mass [3, 4]. Phase separation of polybutadiene (PBD) in the polyamide matrix affects positively the toughness which, with 10 mass% of PBD in the copolymer as compared to unmodified PA 6, is increased by an order of magnitude, whereas the Young modulus and tensile strength at yield are cut as much as by half. With increasing content of the polybutadiene phase, the fraction of amorphous polyamide phase, as well as the equilibrium sorption of water are increased [3, 4].

The present contribution deals with an assessment of thermal properties of block copolymers which, with the given types of copolymers, have not yet been studied in detail.

Experimental

Materials

ε-Caprolactam (CL) from DSM was stored in a desiccator over P_2O_5 and used without purification.

Tolylene diisocyanate (TDI) (Bayer AG, 80:20 mass/mass mixture of 2,4- and 2,6-isomer), was used without any purification.

α,ω-Dihydroxy terminated polybutadiene (DHPBD) with M_n=4900 g mol^{-1}, c_{OH}=0.38 mmol g^{-1} and its reaction product with TDI and CL (PBD.CL) with M_n=6000 g mol^{-1}, were supplied by Synthetic Rubber Research Institute, Kralupy, Czech Republic.

Sodium salt of ε-caprolactam (CLNa) concentrate (from Bruegemann) was stored in a round-bottom flask under protective atmosphere of argon. Content of Na$^+$ was 1.3 mol kg^{-1}.

Preparation of block copolymers

The copolymerizations were carried out by the so-called 'hand casting' method in aluminum molds with wall thickness of 6 mm and internal dimension of 140×150×4 mm, sealed with a gasket of heat-cured silicon rubber, as described in [3].

The polymerization mixtures were prepared under the protective atmosphere of Ar in a glass flask. First, DHPBD was dissolved in molten CL at 110°C. Functionalization agents (TDI) were then introduced into the melt. After heating to 110°C for 1 h, the sodium salt of CL in CL was added, dissolved and the polymerization mixture was transferred into the mold heated to the polymerization temperature. The mold was kept for 30 min in an oil bath at 150°C and then slowly cooled by standing at room temperature. TDI and CLNa were used in equimolar concentrations with respect to the OH group concentration.

Methods

TG measurements were performed using the TGA Q500 instrument (TA Instruments) in the temperature range of 25 to 600°C with a constant heating rate of 10°C min^{-1} or in Hi-Res mode under various experimental conditions; nitrogen purge (60 cm^3 min^{-1}). The measurements under reduced pressure (270 Pa) were carried out on TGA 951 (DuPont Instruments) at a heating rate of 20°C min^{-1} and nitrogen purge (1 cm^3 min^{-1}).

DSC measurements were performed using the DSC Q100 instrument (TA Instruments) in the temperature range of –80 to +250°C with a constant heating rate of 10°C min^{-1} or modulation ±1°C/60 s and a heating rate of 2°C min^{-1}; nitrogen purge (50 cm^3 min^{-1}).

For the DMA measurements, specimens having dimensions of 2×4×30 mm were prepared. For these measurements, we used dry samples or samples conditioned at 52% humidity at 23°C for 110 days. The DMA DX04T tester (RMI, Czech Republic) was used, the measurements being performed in a temperature range between –100 and 250°C at a heating rate of 3°C min^{-1}. Bending mode Single Cantilever with a constant deformation of ±0.2 mm and sinusoidal force at a frequency of 1 Hz was used.

Results and discussion

Using the polymerization casting technique, the poly(ε-caprolactam)-block-polybutadiene copolymers with 5–20% of the PBD phase were prepared. It should be noted that copolymer samples analyzed were not extracted and contained the residue of the initiation system, i.e., the sodium salt of CL (CLNa) and the products of its reaction with air moisture and CO_2.

TG

TG curves of the corresponding homopolymers constituting the block copolymer, that is, the starting α,ω-dihydroxy terminated polybutadiene (DHPBD) and PA 6 (prepared by the anionic polymerization of CL initiated with CLNa and TDI), show in both cases a single-step decomposition, the respective temperatures being 430 and 456°C, Fig. 1. Thus, under given conditions and atmospheric pressure, PBD is thermally more stable than polyamide-6.

The decomposition of the block copolymer sample containing 11.1% of PBD phase is shown in Fig. 2. The curve exhibits two distinct steps: The decomposition rates of the two steps reach their maxima at 320 and 434°C, while the mass drops assume 36 and 61%, respectively. These decreases are not in agreement with the composition of the copolymer (i.e., 11% of PBD and 89% of PA 6 phase) and, similarly, the temperatures of the maximum decomposition rates do not correspond to those of PBD and PA 6, Fig. 1. The mass drop observed up to 240°C (2.9%, Fig. 2) relates to the release of the moisture and unreacted monomer from the sample, and to the degradation of the interblock links. Of all the constitutional parts of the copolymer, it is the carbamate link that exhibits the poorest thermal stability, as illustrated by the curve for PBD.CL in
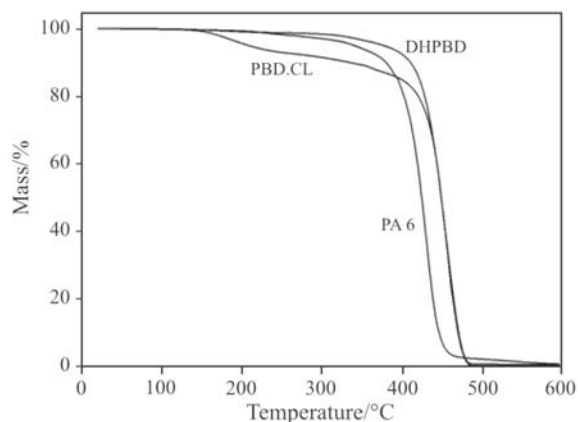

Fig. 1 TG curve of α,ω-dihydroxy terminated polybutadiene (DHPBD), reaction product of DHPBD, tolylene diisocyanate and ε-caprolactam (PBD.CL) and polyamide-6 (PA 6) prepared by the anionic polymerization. Heating rate 10°C min^{-1}, N$_2$ purge 60 cm^3 min^{-1}

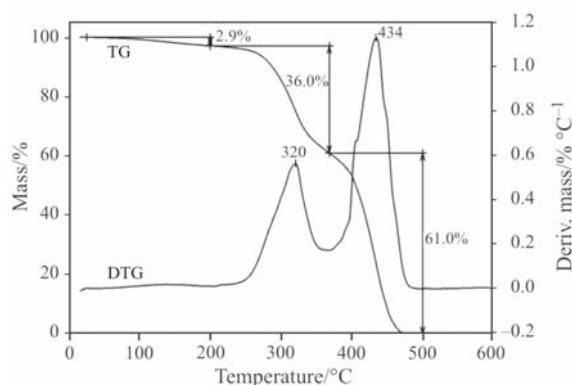**Fig. 2** TG and DTG curves of poly(ε-caprolactam)-block-polybutadiene containing 11.1% of polybutadiene. Heating rate 10°C min^{-1}, N$_2$ purge 60 cm^3 min^{-1}

Fig. 3 TG curves of α,ω-dihydroxy terminated polybutadiene (DHPBD), polyamide-6 (PA 6) and poly(ε-caprolactam)-block-polybutadiene samples with varying content of polybutadiene (PBD), as indicated at curves. Heating rate 20°C min^{-1}, reduced pressure 270 Pa, N$_2$ purge 1 cm^3 min^{-1}

Fig. 1 (the product of the functionalization, reaction of PBD, TDI and CL). It can be concluded that the conventional TG fails to determine the content of the PBD phase in the copolymer.

There are several methods to increase the sensitivity and improve the resolution of TG, as reviewed in [5]. One of them is to perform the TG experiment under reduced pressure and thus to facilitate the desorption of the decomposition products during the analysis. Another possibility is to perform the measurement at a very low rate of heating or to combine heating periods and isothermal lags, etc. Regrettably, the time of analysis is thus enormously prolonged. This drawback can be avoided using the so-called high resolution thermogravimetric analysis (Hi-Res^{TM} TGA).

The TG measurements using the TA 951 module were performed under reduced pressure (270 kPa) which facilitates the release of the degradation products from the sample during the course of its degradation. Although the measurement itself is rather time-consuming, especially the preparation stage preceding the analysis, the results thus obtained were encouraging. The maximum rate of the decomposition curve of polyamide-6 was distinctly shifted toward lower temperatures (as much as by 130°C, closer to the melting point of PA 6), as follows from the comparison of the curves for PA 6 in Figs 1 and 3. When temperature exceeds the melting point of the PA 6 (220°C), then, due to the depolymerization speeded up by the presence of a base, the content of CL is increased, and resorption of CL under reduced pressure is rapid. This is in accordance with reported data [6]: A depolymerization resulting in CL formation and random chain scission was demonstrated for the degradation of PA 6, using TG coupled with a proper detection of degradation products (mass and FTIR spectroscopies), water, carbon dioxide and 5-hexene-amide were the degradation by-products. The decomposition of DHPBD proceeded similarly as under normal pressure, cf. Figs 1 and 3.
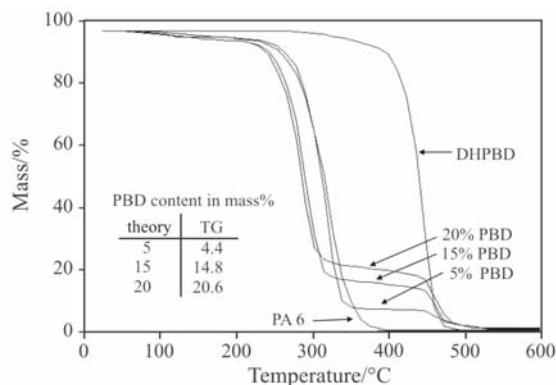
The technique (TG under reduced pressure) was applied also to measurements of the thermal stability of block copolymers (Fig. 3). The decomposition proceeded in two steps, showing separated processes of both components constituting the block copolymer. Using a standard evaluation of the mass drop related to the second step, the results obtained agreed very well with the content of the elastic phase in the copolymer.

Further, thermal behavior of the block copolymers was studied by high resolution TG using Q500-HiRes TGA^{TM} instrument (TA Instruments). In this experimental set up, the heating rate was adapted to the degradation rate (the changes of sample mass) according to manually adjusted parameters (sensitivity and resolution). The values of these parameters affect the shape of the thermogravimetric curve [5].

Figure 4 presents HiRes TG curves for the block copolymer containing 11.1% of elastic blocks for var-
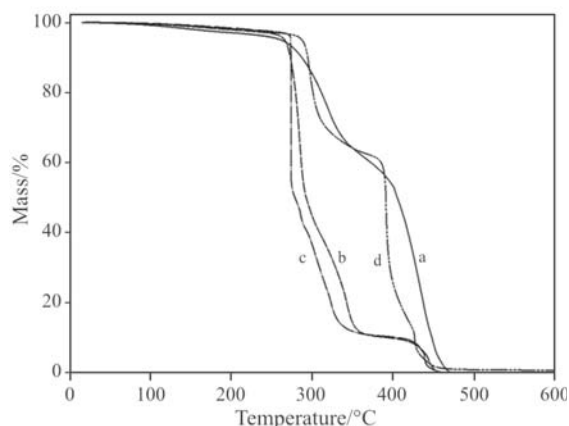

Fig. 4 TG curves of poly(ε-caprolactam)-block-polybutadiene containing 11.1% of polybutadiene obtained by a – conventional TG at a heating rate 10°C min^{-1} and from Hi-Res^{TM} TGA, b – heating rate 20°C min^{-1}/sensitivity 1/resolution 4°C, c – 20/3/4, d – 30/1/4, N$_2$ purge 60 cm^3 min^{-1}
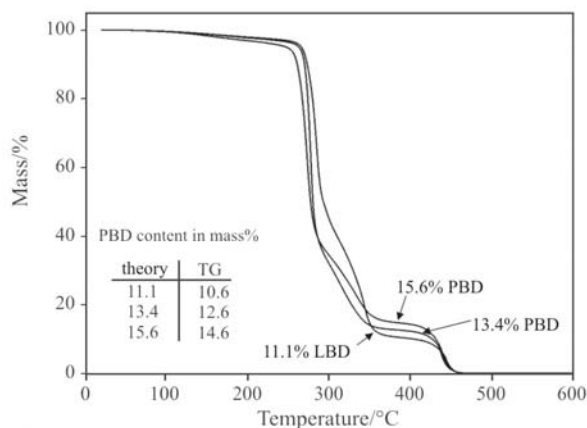
Fig. 5 Hi-Res TG curves of poly(ε-caprolactam)-block-polybutadiene with varying content of polybutadiene (PBD), as indicated at curves. Heating rate 20°C min⁻¹, sensitivity 1, resolution 4°C, N₂ purge 60 cm³ min⁻¹

ious regimes of measurement including that of a constant heating rate (conventional TG). When experimental conditions used for curves b and c had been applied to copolymers with varying content of the PBD phase, a very good agreement was found between the content of PBD in the polymerization feed and that determined by Hi-Res™ TGA, cf. Fig. 5.

DSC

A block copolymer sample containing 13.4% of PBD was subjected to the conventional DSC experiment (Fig. 6). From the curve obtained, the values of T_g cannot be determined reliably for both phases. A melting endotherm was found at 211°C, yielding melting enthalpy of 68.2 J g⁻¹. When related to the PA 6 phase, it assumes a value of 79 J g⁻¹ which corresponds to 42% of crystalline fraction (a value of ΔH_m for 100% crystalline PA 6 190 J g⁻¹ was taken from reference [7]). Only when modulated DSC (TMDSC) was utilized (Fig. 7), T_g of the PBD phase (–48°C) and indistinct T_g of the PA 6 phase (~25°C) could be detected. To get more reliable values of T_g of PA 6 phase, the copolymer sample was annealed for 5 min at 240°C, and then the pan containing the sample was quenched in liquid nitrogen. TMDSC trace for the copolymer after quenching is shown in Fig. 8. The values of T_g of the PA6 and PBD phases thus obtained were 38 and –47°C, respectively, the latter being identical with that from Fig. 7. The TMDSC method enables one to divide the overall heat flow into reversible and irreversible component. On the overall and reversible traces, following the T_g of the PA 6 phase, an exotherm of its cold crystallization appears with a maximum at 57°C.
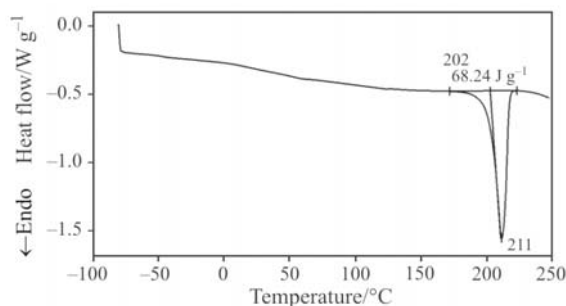

Fig. 6 DSC traces of poly(ε-caprolactam)-block-polybutadiene containing 13.4% polybutadiene. Heating rate 10°C min⁻¹, N₂ purge 50 cm³ min⁻¹
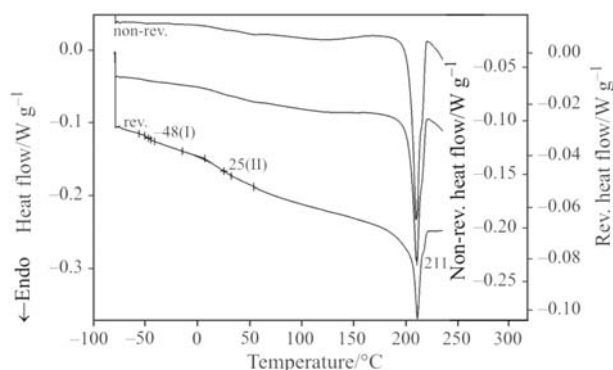

Fig. 7 TMDSC traces of poly(ε-caprolactam)-block-polybutadiene containing 13.4% polybutadiene, virgin sample. Heating rate 2°C min⁻¹, sin modulation ±1°C/60 s, N₂ purge 50 cm³ min⁻¹
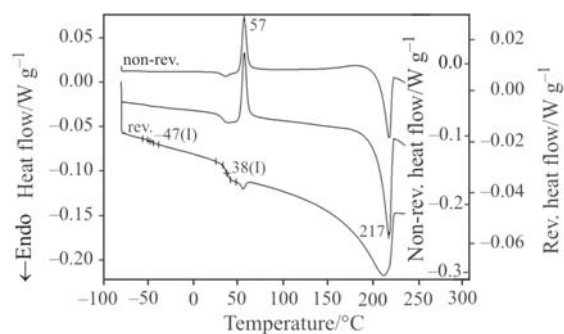

Fig. 8 TMDSC traces of poly(ε-caprolactam)-block-polybutadiene containing 13.4% polybutadiene, quenched sample. Heating rate 2°C min⁻¹, sin modulation ±1°C/60 s, N₂ purge 50 cm³ min⁻¹

DMA

T_g can more sensitively be determined by DMA. The dependence of the tangent of the loss factor (tgδ) of virgin sample (i.e., after polymerization) on temperature shows two distinct maxima (Fig. 9). One of them, located at –34°C, corresponds to T_g of the PBD phase while the other one (73°C), referred to as α-transition, corresponds to T_g of the PA 6 phase.
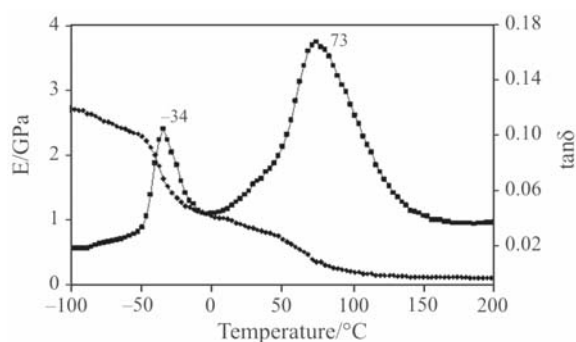
Fig. 9 Dynamic mechanical spectra of dry sample (virgin) of poly(ε-caprolactam)-block-polybutadiene containing 13.4% polybutadiene
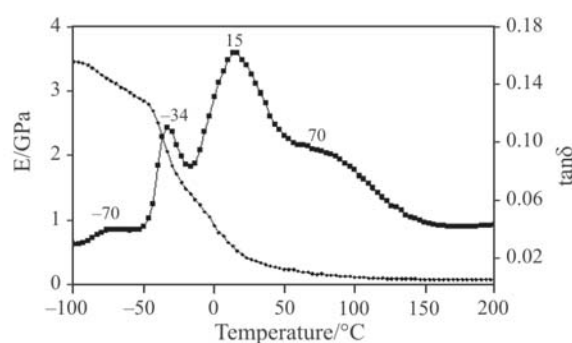

Fig. 10 Dynamic mechanical spectra of conditioned sample (52 rel.% humidity, 20°C, 110 days) of poly(ε-caprolactam)-block-polybutadiene containing 13.4% polybutadiene

In case of the conditioned sample (52% relative humidity, 110 days), another maximum appears on the DMA curve (Fig. 10). The first one is located at –70°C (not distinct in Fig. 9) and can be assigned to the well-known β-transition of polyamide chains caused by the enhanced mobility of the –CO–NH– bonds in the polymer. The second one is attributed to T_g of PBD (–34°C). The α-transition (at 73°C, cf. Fig. 9) is split to 15 and 70°C which may suggest the presence of two non-crystalline phases (one being less plasticized), wherein the intensity of the latter is very low. Similar phenomenon was observed in case of DMA of polyesteramides [8].

Conclusions

Poly(ε-caprolactam)-block-polybutadiene copolymers were characterized by thermoanalytical methods.

Only TG performed under reduced pressure and Hi-Res TG were able, applying properly adjusted parameters, to distinguish the decomposition of the two components of the block copolymer and to determine their content. Of all parts of the block copolymer, the

carbamate links, connecting polybutadiene and polyamide blocks, show the lowest thermal stability. The polyamide phase represents the component with a lower thermal stability than the polybutadiene one.

Conventional DSC could only be used to determine the melting temperature and melting enthalpy of the polyamide phase. By using TMDSC, glass transition temperature of the polybutadiene phase was detected while T_g of the polyamide phase was measured after the quenching of the sample.

DMA confirmed unambiguously the presence of both components of the block copolymer. The value of T_g of the PA 6 phase was affected by atmospheric water sorption.

Values of glass transition temperature of the block copolymer components found by DSC differ from those determined by DMA, the differences being caused by dissimilar heating rates, geometries of samples and thermal history.

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