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Multiblock polyurethanes containing butadiene-co-acrylonitrile oligomers as soft segments

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Summary

Amorphous segmented polyurethanes (PUs) were prepared by a solution two-step synthesis from 2,4-toluenediisocyanate, 1,4-butanediol and ATBN, a telechelic butadiene-acrylonitrile oligomer. The composition was varied in the range 11-61% by wt of ATBN. The copolymers were characterized by elemental analysis, viscosity measurements and FTIR and ^{1}H-NMR spectroscopy. Differential scanning calorimetry and dynamic mechanical thermal analysis showed the presence of two separate glass transitions for hard and soft segments, thus indicating a two phase behaviour of the investigated PUs. Evidence of interphase interactions was not found. The dynamic mechanical spectra suggested the occurrance of a phase inversion from a hard segment matrix to a soft segment continuous phase when the ATBN content is 38% by wt or higher.

Introduction

Segmented polyurethanes (PUs) are linear block copolymers consisting of alternating rigid and flexible segments. The rigid segments are polar urethane oligomers formed by reacting diisocyanates and short chain diols, while the flexible segments are usually polyether or polyester telechelic oligomers having hydroxyl end-groups. The different polarity of the blocks and the extensive hydrogen bonding interaction among urethane groups induces a phase separation into "hard" and "soft" domains. The nature of the segments and the composition affect the degree of phase separation, the interphase mixing and the domain organization, thus determining the physical-mechanical properties of these copolymers(1). There is currently a growing interest in PUs containing polybutadiene (2) or butadiene based(3) soft segments because of their low moisture permeability, high hydrolitic stability and improved resistance to oxidation. In this work we report on the preparation and characterization of multiblock PUs containing hard segments built up from 2,4-toluenediisocyanate (TDI) and 1,4-butanediol (BDL), and a butadiene-acrylonitrile oligomer with secondary amino end-groups (ATBN) as soft segment. ATBN has been previously used as the rubbery component in multiblock amide-rubber(4) and imide-rubber(5) copolymers.

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Experimental

Materials

TDI (Fluka) was a 80/20% mixture of 2,4 and 2,6 isomers and was distilled in vacuo before use. BDL (Fluka) was dried overnight over anhydrous calcium chloride and was purified by vacuum distillation. ATBN, kindly provided by Goodrich Chemical Italia, had 17% by wt of acrylonitrile, MW of approx. 3500 and functionality close to 2. The oligomer was freed from some unreacted N-aminoethyl-1,4-piperazine according to the following procedure: a dichloromethane solution of ATBN was eluted through neutral aluminum oxide and, after removal of the solvent, the residue was kept at 60°C and 10^{-3} mmHg for 24 h. Tetrahydrofuran (THF) was refluxed for 4 h over sodium wire in the presence of benzophenone and distilled before use.

Techniques

The IR spectra were obtained on thin films prepared by evaporation of THF solutions of the polymer using a Bruker IFS 66 FTIR instrument. The ^{1}H-NMR spectra were obtained at 30°C on chloroform-d solutions of the polymer containing a few drops of trifluoroacetic acid-d and TMS as internal standard using a Bruker AC 270 spectrometer operating at 270 MHz. The viscosity measurements were taken in N,N-dimethylacetamide (DMA) at 25°C , c=0.5 g/dL using an Ubbelhode viscometer. A Mettler TA 3000 instrument was used for the DSC. The thermograms were obtained on 8-10 mg of sample at a heating rate of 10°C/min. The glass transition temperature was taken as the midpoint of the transition step in the second scan. Test specimens for the dynamic mechanical thermal analysis, DMTA, 0.3-0.4 mm thick, were prepared by compression molding at 150°C. The specimens were run on a Polymer Laboratories PL-DMTA MKII instrument with a 10 Hz frequency from -100°C to 150°C at a heating rate of 4°C/min.

General Polymerization Procedure

Copolymers of different composition were obtained varying the ATBN/BDL molar ratio according to the following general procedure. A solution of ATBN, x mmol, in 10 mL of THF was added dropwise at room temperature to 3.48 g, 20.0 mmol, of TDI dissolved in 20 mL of THF. The temperature was slowly raised to 70°C and the mixture was reacted for 1 h. Then 20 mg of catalyst, dibutyltindilaurate, and 20.0-x mmol of chain extender, BDL, in 10 mL of THF were added dropwise and the reaction was continued for 2 h. The polymer was precipitated in water, washed repeatedly with water and methanol and dried at 60° C under vacuum for 24 h. The polymers were purified from unreacted ATBN or rubber rich oligomers by refluxing with benzene for 3 h. The benzene soluble fraction was 2-8% by wt.

Results and Discussion

Synthesis and Characterization

The copolymers were prepared in two steps using the solution technique in order to prevent phase separation during the synthesis and to ensure a nearly statistical distribution of chain length in the PU blocks. A butadiene-acrylonitrile oligomer having secondary amino groups as chain ends (ATBN) was first reacted in THF with a large molar excess of TDI to give isocyanate end-capped ATBN. In the chain extension step the polyurethane blocks were built up reacting the mixture containing the excess of TDI and the -NCO end-capped ATBN with the stoichiometric amount of BDL. It is reasonable to assume that under these homogeneous conditions the actual structure of the copolymers consists of alternating monodisperse ATBN blocks linked by urea groups to polydisperse PU blocks having a statistical distribution of segment length. The average size of the hard blocks depends on the copolymer composition which is determined by the molar excess of TDI in the first step. PUs containing 11-61 wt% of soft segments (SS) were prepared using an ATBN having 17 wt% of acrylonitrile and a MW of approx. 3500. The results of the synthesis are reported in Table 1 together with some characterization data of the copolymers. The number in the polymer code indicates the wt% of SS as determined by elemental analysis. The pure hard segment (HS) homopolymer, PU-0, was prepared in the same way as the copolymers. A high MW poly(butadiene-*co*-acrylonitrile) sample, PU-100, was prepared from TDI and ATBN as a model of the pure SS domains. The crude copolymers were extracted with benzene in order to remove traces of unreacted ATBN and/or ATBN rich oligomers. All the copolymers are soluble at room temperature in strongly polar solvents such as DMA, *m*-cresol, THF and N-methyl-2-pyrrolidone (NMP). Tough and flexible films can be obtained either from solutions or by compression molding in the case of copolymers having an SS content higher than 28%. PU-0, PU-11 and PU-28 films are rigid and brittle.

The PUs were characterized by IR and ^{1}H-NMR spectroscopy. The IR spectra of PUs show the bonded NH stretching band at 3300 cm^{-1} with a small shoulder at 3440 cm^{-1} representing the free NH stretching band. The intensity ratio of these bands is independent from the copolymer composition and is unaffected by annealing. Hydrogen bonded carbonyl stretching occurs at 1700 cm^{-1} whereas the corresponding band of the free CO appears as a shoulder at 1740 cm^{-1}(6). Other characteristic absorptions of the HS are : 1600 cm^{-1} (C-C st of the aromatic ring), 1530 and 1240 cm^{-1} (amide II and III respectively) and 1075 (COOC st). The incorporation of ATBN was confirmed by the

Table 1. Synthesis and Characterization of Segmented PUs

Polymer code	wt% of ATBN calc[a]	wt% of ATBN found[b]	Yield %	η_{inh} dL/g[c]	Elemental Analysis C	H	N
PU-0	0	-	93	0.68	59.28	6.51	9.85
PU-11	15	11	90	0.49	61.37	6.57	9.64
PU-28	30	28	93	0.72	65.81	7.22	8.96
PU-38	40	38	92	0.79	67.46	7.45	8.66
PU-51	50	51	96	0.73	70.12	8.20	8.12
PU-61	60	61	90	0.86	71.53	8.25	8.02
PU-100	100	-	88	-	-	-	-

a) From the reagent molar ratios; b) from elemental analysis; c) in DMA at 25°C, c=0.5 g/dL.

presence of the bands at 2220 cm^{-1} (CN st) and at 970, 910 cm^{-1} (C=C bending of 1,4-trans and 1,2 units of butadiene, respectively). Figure 1 shows the ^{1}H-NMR spectrum of PU-38 along with the assignment of the main resonances made on the basis of the spectra of the SS and HS models and of literature data. The spectra are in line with the proposed structure. Using the integrated intensities of the appropriate resonances it was found that most of butadiene units (>75%) are in the 1,4 enchainment(7).

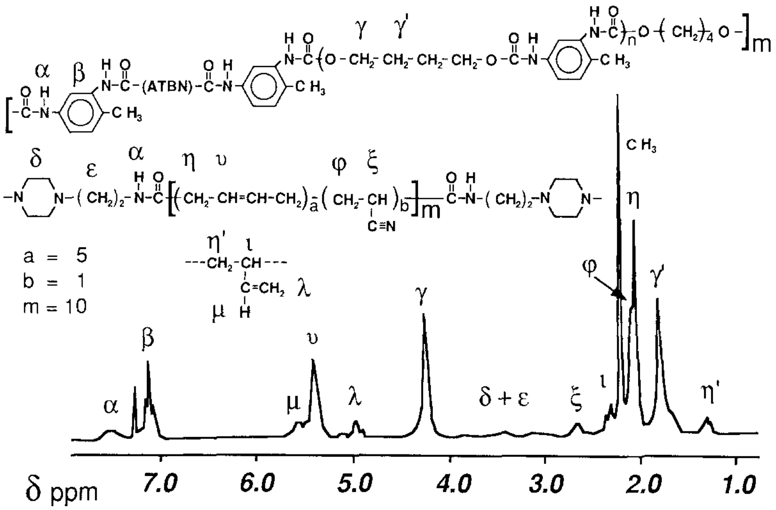

Figure 1. 270 MHz ^{1}H-NMR spectrum of PU-38 in $CDCl_3/CF_3COOD$

Thermal Analysis

In Figure 2 are reported the DSC traces of PU-0, PU-100 and of some selected copolymers. All copolymers are amorphous confirming the literature data on TDI based PUs(2), as shown by the absence of first order transitions up to 300°C. The thermal data are summarized in Table 2. The presence of two glass transitions clearly indicates a two-phase behaviour of

Table 2. DSC Data for PU Copolymers and for PU-0 and PU-100

Polymer Code	Tg1, °C,	Tg2, °C,
PU-0	-	98
PU-11	-50	97
PU-28	-47	97
PU-38	-48	85
PU-51	-50	a)
PU-61	-48	a)
PU-100	-47	-

a) Broad and ill defined transition in the range 60-100°C.

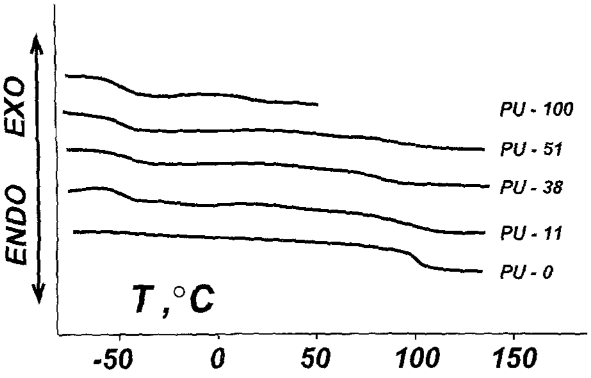

Figure 2. DSC thermograms of some PU copolymers and of PU-0 and PU-100 homopolymers.

all copolymers. The low temperature glass transition, Tg1, attributed to the soft ATBN phase, is well defined and occurs in the -47/-50°C temperature range for all the copolymers. The closeness of these transitions to that of PU-100 (-47°C) suggests that phase separation of SS is almost complete and that the eventual presence of HS in the soft phase should be negligeable. Thus Tg1 is rather insensitive to changes in composition, as expected by the absence of specific interactions between SS and HS(2). A broad high temperature transition arising from the urethane hard phase is clearly detectable in the case of PU rich copolymers and becomes better defined following a first heating-cooling cycle. It is likely that this phenomenon is due to a rearrangement of the interphase boundary during the first scan. The Tg2 values of the copolymers are quite close to that of PU-0 when the SS content is lower than 28% by wt. It was impossible, however, to detect any meaningful glass transition of the HS for SS rich PUs because it takes place over a wide range of temperatures. This behaviour may be attributed to the polydispersity of the hard blocks and to the lowering of their average length as the ATBN content increases. It is also possible that some ATBN units are trapped in HS domains when the HS average length is small.

Dynamic Mechanical Thermal Analysis

The dynamic storage modulus and loss tangent of some segmented PUs and of the PU-0 and PU-100 homopolymers are plotted as a function of the temperature in Figure 3. The relevant dynamic mechanical data are reported in Table 3. The relaxation behaviour clearly confirms the two phase structure of the copolymers. Two separate relaxation phenomena, indicated by a decrease in the storage modulus and a corresponding tanδ peak, are in fact found in the dynamic mechanical spectra. The glass transition temperatures found by DMTA are about 20°C higher than those found by DSC.

Table 3. Dynamic Mechanical Properties of PU Copolymers and of PU-0 and PU-100 Homopolymers

Polymer Code	Tg1 °C	Tg2 °C	tanδ1	tanδ2	logE' at +30°C
PU-0	-	122	-	1.36	8.90
PU-11	-32	120	0.14	1.20	8.65
PU-28	-29	120	0.30	0.72	8.35
PU-38	-28	120	0.58	0.58	7.55
PU-51	-27	118	0.68	0.40	7.42
PU-61	-27	-	0.68	-	7.30
PU-100	-34	-	1.10	-	6.63

The general trend of both Tgs is, however, the same. The value of the plateau modulus for Tg1<T<Tg2 increases as the content of hard segments increases (see Table 2). For ATBN rich copolymers this effect is likely due to a reinforcing effect of the HS domains. The difference between the E' values of PU-38 and PU-28, ≈ 0.8 order of magnitude, is, however too high to reflect only the change in the relative amount of the two phases and suggests a different morphology for the two samples. This hypothesis is supported by a comparison between the maxima of the tanδ peaks of SS and HS domains for PU-38

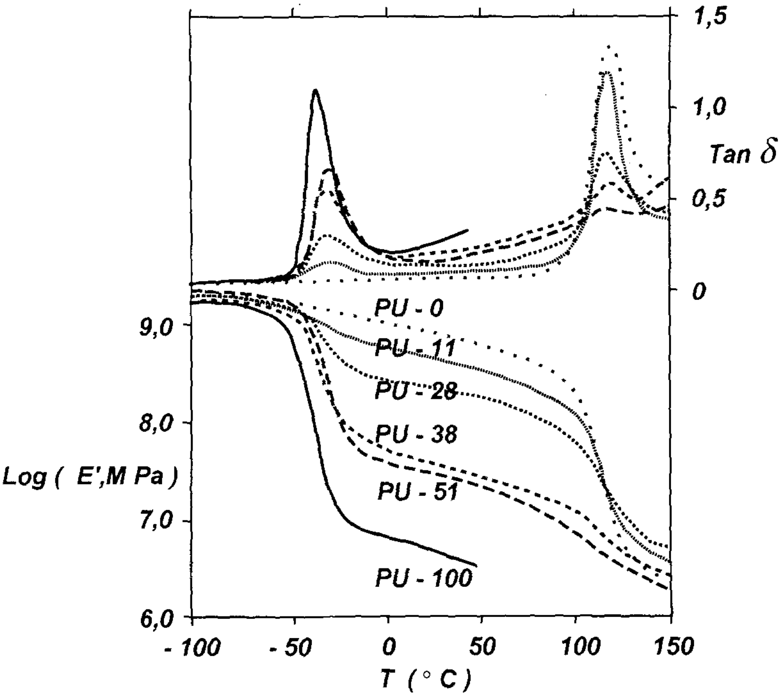

Figure 3. Temperature dependence of the storage modulus and of the loss tangent for segmented PUs and for PU-0 and PU-100.

and PU-28. We suggest that starting from 38% by weight of SS content, corresponding to 46% by volume, a phase inversion occurs, which leads to a continuous soft-segment phase.

In conclusion, for the ATBN-urethane multiblock copolymers investigated both DSC and DMTA results indicate an almost complete microphase segregation of HS and SS, as previously reported for other segmented PUs containing diene oligomers as SS(2). An inversion of the continuous and dispersed phases in the range 28-38% by wt of soft segment is responsible for the more significant changes in the dynamic mechanical properties of PUs of different composition.

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