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Synthesis and preliminary characterization of rubber-polyamide multiblock copolymers

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Summary

"Hard-soft" multiblock copolymers, $(AB)_n$ type, have been prepared by incorporating rubbery segments into a polyamide 6,10 chain according to a two steps procedure. As soft segments, telechelic polybutadiene or poly(butadiene-co-acrylonitrile) oligomers have been used. The prepared copolymers have been characterized by IR spectroscopy and differential scanning calorimetry. Two different and well defined glass transitions have been observed indicating a phase segregation for the rubbery and polyamide segments.

Introduction

Changes in physical, thermal and mechanical properties of polyamides can be accomplished by incorporating along the polyamide chain "soft" segments able to increase the chain flexibility. The properties of the resulting "hard-soft" multiblock copolymer depend on the nature of the flexible segment as well as on the relative amount and on the average size of the heterotype blocks.

α,ω-Carboxy polybutadiene and α,ω-dihydroxy poly(oxyethylene) have been incorporated as "soft" segments in poly(4,4'-oxy-di-p-phenylene-isophtalamide) and poly(hexamethylene adipamide) chains respectively.(1,2) A microphase separation and an improvement of the overall chain flexibility with respect to the parent polyamides were observed for the above copolymers.

The present paper deals with the preparation and a preliminary characterization of "hard-soft" multiblock copolymers containing poly(hexamethylene sebacamide) (PA 6,10) as hard segment and polybutadiene or poly(butadiene-co-acrylonitrile) as soft segment.

Experimental

Materials: Poly(butadiene-co-acrylonitrile) -COOH terminated, (CTBN, 1300 x 15), =NH terminated (ATBN, 1300 x 21) and -OH terminated (HTBN, 1300 x 29) were kindly supplied by Goodrich Chemical Italia. All these copolymers have an acrylonitrile content of 10% by wt, a molecular weight of about 3500 and a functionality close to 2.

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Polybutadiene hydroxyl terminated (HTB, MW=2800) was purchased from Polysciences.

ATBN was purified from residual N-aminoethylpiperazine according to the following procedure:a sample was dissolved in methylene chloride,the resulting solution was filtered and the solvent was removed under vacuum.The recovered product was kept under high vacuum (10^{-2} mm Hg) at 80°C during 14 h.

CTBN,HTBN and HTB were vacuum treated (10^{-2} mm Hg) at 80°C for 4 h to remove volatile byproducts. Sebacoyl chloride (Fluka Reagent) was purified by fractional distillation before use. 1,6-Diaminohexane (HMD) was purified by crystallization in anhydrous toluene under nitrogen.Solvents,when required,were purified according to the standard procedures.

Techniques

The thermal data were obtained on melt pressed samples (8÷10 mg) by using a Mettler DSC 20 differential scanning calorimeter.

IR analysis was carried out on films prepared by melt casting and the spectra were recorded on a Perkin-Elmer 457 Spectrophotometer.

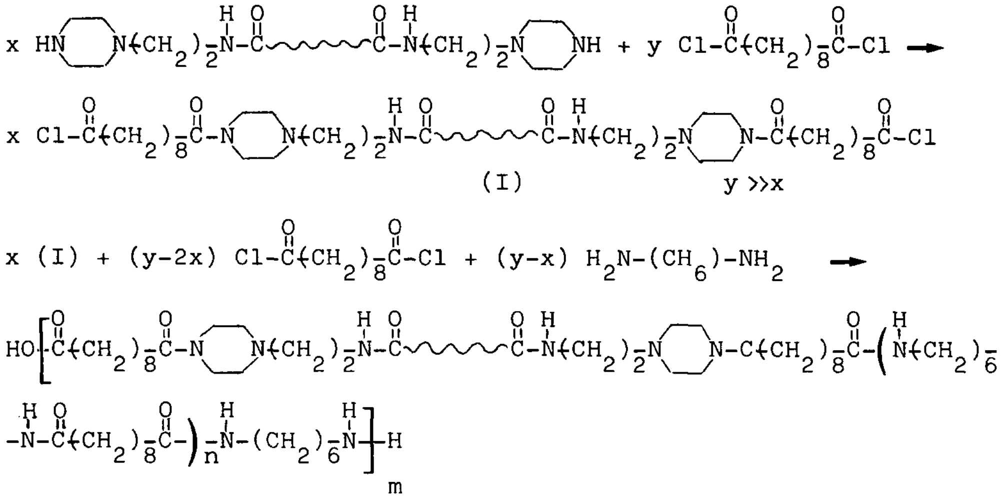
Typical Synthesis procedure:preparation of HTBN-PA 6,10 copolymer.

HTBN (5.25 g;1.50 mmol) and triethylamine (0.30 g;3.0 mmol) dissolved in 30 mL of anhydrous chloroform were added dropwise, at 50°C, to 10 mL of a $CHCl_3$ solution containing sebacoyl chloride (4.78 g; 20.0 mmol) under stirring,in nitrogen atmosphere. Triethylamine hydrochloride was formed and the stirring was continued for 1 h. The resulting solution was subsequently added quickly and under vigorous stirring in a Waring Blendor to 370 mL of a water solution containing 2.15 g (18.5 mmol) HMD and 1.48 g (37.0 mmol) NaOH.After stirring for 5 min the polymer was collected on a filter glass,repeatedly washed with water and dried under vacuum at 50°C (9.86 g; 92% yield).

Results and Discussion

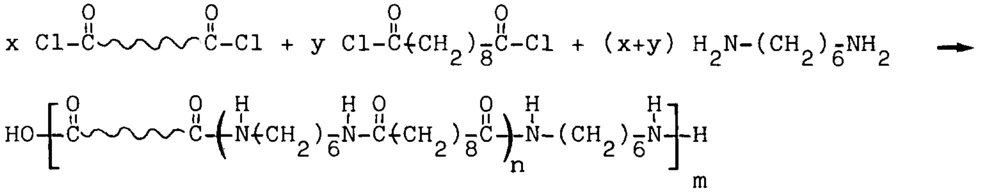
"Hard-soft" multiblock copolymers were synthesized keeping the relative amount of the heterotype blocks in the feed constant (about 1:1 by wt). In all the cases sebacoyl dichloride and 1,6-diaminohexane were used to build up the PA 6,10 segments while for the soft segments telechelic oligomers of polybutadiene or poly(butadiene-co-acrylonitrile) having MW in the range 2800-3500 were used. The reaction schemes reported below show the different procedures followed to obtain copolymers according to the nature of the functional groups of the rubbery oligomers.

Procedure A: use of amino terminated poly(butadiene-co-acrylonitrile):



Procedure B: use of carboxyl terminated poly(butadiene-co- acrylonitrile).

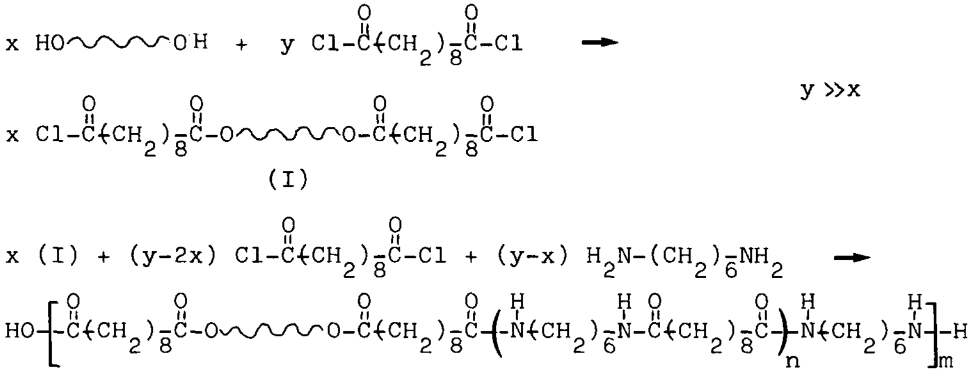
The dichloride of CTBN,prepared according to the standard procedures,is used in the synthesis.



$$x\ Cl-\overset{\overset{O}{\|}}{C}\sim\sim\sim\sim\overset{\overset{O}{\|}}{C}-Cl + y\ Cl-\overset{\overset{O}{\|}}{C}(CH_2)_8\overset{\overset{O}{\|}}{C}-Cl + (x+y)\ H_2N-(CH_2)_6NH_2 \longrightarrow$$

$$HO\left[\overset{\overset{O}{\|}}{C}\sim\sim\sim\sim\overset{\overset{O}{\|}}{C}-\left(\overset{\overset{H}{|}}{N}(CH_2)_6\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}(CH_2)_8\overset{\overset{O}{\|}}{C}\right)_n\overset{\overset{H}{|}}{N}-(CH_2)_6\overset{\overset{H}{|}}{N}\right]_m H$$

Procedure C: use of hydroxyl terminated poly(butadiene-co-acrylonitrile) or polybutadiene.



$$x\ HO\sim\sim\sim\sim OH + y\ Cl-\overset{\overset{O}{\|}}{C}(CH_2)_8\overset{\overset{O}{\|}}{C}-Cl \longrightarrow$$

$$x\ Cl-\overset{\overset{O}{\|}}{C}(CH_2)_8\overset{\overset{O}{\|}}{C}-O\sim\sim\sim\sim O-\overset{\overset{O}{\|}}{C}(CH_2)_8\overset{\overset{O}{\|}}{C}-Cl \quad (I) \qquad y \gg x$$

$$x\ (I) + (y-2x)\ Cl-\overset{\overset{O}{\|}}{C}(CH_2)_8\overset{\overset{O}{\|}}{C}-Cl + (y-x)\ H_2N-(CH_2)_6NH_2 \longrightarrow$$

$$HO\left[\overset{\overset{O}{\|}}{C}(CH_2)_8\overset{\overset{O}{\|}}{C}-O\sim\sim\sim\sim O-\overset{\overset{O}{\|}}{C}(CH_2)_8\overset{\overset{O}{\|}}{C}\left(\overset{\overset{H}{|}}{N}(CH_2)_6\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}(CH_2)_8\overset{\overset{O}{\|}}{C}\right)_n\overset{\overset{H}{|}}{N}(CH_2)_6\overset{\overset{H}{|}}{N}\right]_m H$$

In all the procedures,the building up of the polyamide blocks has been carried out by a low temperature stirred interfacial polycondensation.Reaction schemes analogous to B and C have been previously used in the synthesis of block polyamidoesters and polyamidoethers.(3,4).

The prepared copolymers were extracted with benzene before characterization. The benzene soluble fraction (1-6 % by wt) consist of oligomers which are very rich in rubbery component as shown by the IR spectra (vide infra).The yields,calculated after extraction, are in the range 75-89%. It is to be remarked that the copolymer's architecture is of a random multiblock type,$(AB)_n$ and the sizes of the polyamide blocks are polydisperse.
The prepared copolymers,together with their main characteristics, are reported in Table 1.
The chemical composition was calculated on the basis of the elemental analysis. The structure was checked by IR analysis.
A common feature of all the IR spectra is the presence of bands characteristic of amide groups (3300 cm^{-1} ν -NH; 1635 cm^{-1} and 1540 cm^{-1} amide I and II bands respectively) and of butadiene units (965 cm^{-1} 1,4-trans; 910 cm^{-1}, 1,2-vinyl). A weak band due to the -C≡N stretching at 2235 cm^{-1} was also observed in the case of copolymers prepared from ATBN,HTBN and CTBN. The links between hard and soft segments could be evidenced,in the case of copolymers prepared from -OH terminated rubbers (HTB,HTBN), by the presence in their spectra of a band at 1735 cm^{-1}, attributed to the -C=O stretching of the ester groups.
The prepared copolymers are practically insoluble either in typical solvents of polyamides such as m-cresol and formic acid or in good rubber solvents (benzene,chloroform,dimethylacetamide). Extensive swelling in some of these solvents or in their mixtures was observed. This behaviour can be explained on the basis of substantial differences in the values of solubility parameters of the rubbery and polyamide blocks (8÷9 δ and 13 δ respectively). (5). HTBN-PA 6,10 only is rather soluble in m-cresol and a reliable determination of the inherent viscosity was therefore possible: η_{inh} = 0.88 dL/g (25°C, c= 0.050 g/dL). The copolymers can easily be compression molded at 250°C to highly flexible and tough films. The thermal data,obtained by

Table 1 : Prepared PA 6,10-rubber copolymers.

Polymer code	Composition a) (wt % of rubber)	wt % of benzene soluble fraction	Yield (wt %)
HTBN-PA 6,10	48	5.2	87
ATBN-PA 6,10	50	0.8	88
CTBN-PA 6,10	47	6.4	75
HTB -PA 6,10	49	3.0	89

a) determined on the basis of the elemental analysis.

Table 2 : Thermal Data of the Prepared Copolymers

Polymer code	Tm (°C)	ΔHm [a)] J/g	Tg [b)] (°C)
HTBN-PA 6,10	217	24	-57; +40
ATBN-PA 6,10	217	22	-58; +38
CTBN-PA 6,10	212	28	-58; +35
HTB -PA 6,10	216	12	-64; +40
PA 6,10	220	58	- ; +40

a) apparent enthalpy of fusion

b) midpoint of the glass transition step.

differential scanning calorimetry on such films, are reported in Table 2. A typical thermogram is shown in Figure 1 for CTBN-PA 6,10 as an example. The temperature corresponding to the maximum of the endotherm is 212°C and may be related to the melting of a cristalline phase built up by the polyamide blocks. The two different glass transitions at -58°C and +35°C can be attributed to the rubbery and to the amorphous polyamide phases respectively. Very similar thermograms were observed in the case of the other copolymers as indicated by the data of Table 2 where for sake of comparison, the thermal data observed for a sample of pure PA 6,10 prepared under experimental conditions analogous to those used for the synthesis of the copolymers are also reported. The presence of two well defined glass transitions indicates a phase segregation phenomenon of the rubbery and polyamide segments, as expected on the basis of their respective solubility parameters.

The melting temperatures of PA 6,10 phase and the ΔHm values are comparable with those of the PA 6,10 homopolymer and are scarcely influenced by the type of rubber employed,except in the case of HTB which presents the lowest value of melting enthalpy. The average length of PA blocks,which is about 10 repeat units as calculated from the MW of the rubbery segments and from the composition,is consistent with the formation of PA

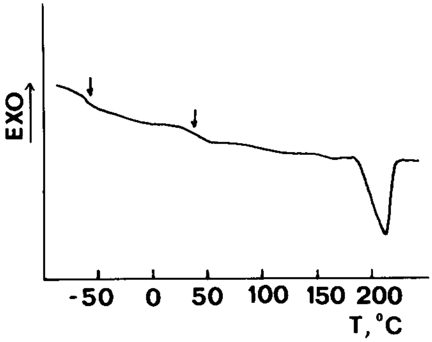


Figure 1: DSC thermogram of the CTBN-PA 6,10 copolymer. The arrows show the two glass transitions.

crystallites and well accounts for high melting temperatures and high enthalpies of fusion observed for the block copolymers.

Results on the synthesis and characterization of polyamide-rubber block copolymers having different amounts of incorporated rubber and on their dynamic-mechanical and thermal properties will be reported in a forthcoming paper.

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