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Synthesis and Characterization of Nylon-Polyisobutylene-Nylon Triblock Copolymers

I. Preliminary Studies

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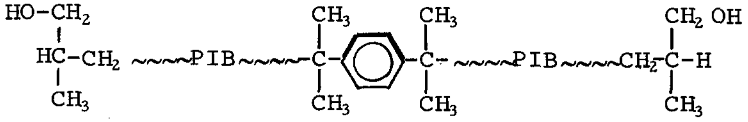
Abstract

Nylon-6-polyisobutylene-nylon-6 triblock copolymers have been synthesized by converting telechelic polyisobutylene diols to α,ω-diisocyanate polyisobutylenes and using these macroactivators, in conjunction with strong base, to induce the subsequent anionic polymerization of ε-caprolactam. Pure block copolymer was obtained by suitable sequential extraction. Products were characterized by composition, molecular weight and DSC.

Introduction

The efficient synthesis of terminally bifunctional (telechelic) polyisobutylenes, particularly the telechelic polyisobutylene diol



$HOCH_2-PIB-CH_2OH$

by the inifer technique (KENNEDY and SMITH, 1979; KENNEDY et al. 1979; IVAN et al. 1980a) has opened numerous avenues toward the preparation of many novel polymers and sequential copolymers. In the course of fundamental investigations with telechelic polyisobutylene diols the thought occurred to us that new poly(caprolactam-b-isobutylene-b-caprolactam), i.e., nylon-6-PIB-nylon-6, triblock copolymers could be obtained by converting the primary diol termini to isocyanate termini and using these telechelic polyisobutylene diisocyanates, OCN-PIB-NCO, to induce the

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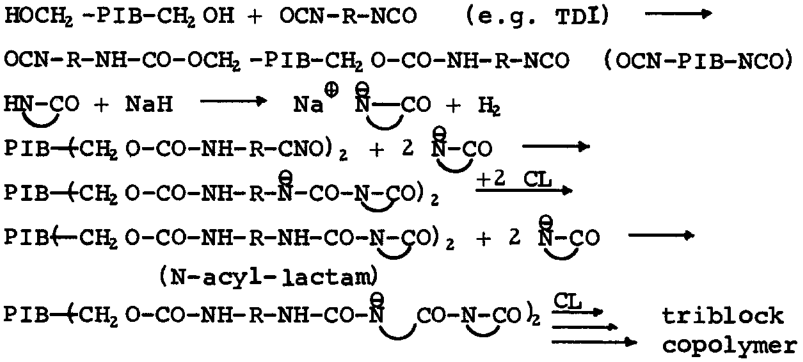
anionic polymerization of ε-caprolactam CL in the presence of strongly basic catalysts, e.g. NaH. The following set of equations helps to visualize the synthesis plan:



This preliminary communication concerns the demonstration of the synthesis and characterization of new nylon-6-PIB-nylon-6 triblock copolymers by this route. The preparation of the telechelic PIB prepolymers carrying -NCO termini OCN-PIB-NCO was carried out by the use of toluene-2,4-diisocyanate TDI in the first step. The strong base initiated polymerization of CL to nylon-6 is extremely slow, however, can be accelerated by the use of promoters which form N-acyl-lactams (see for example ŠEBENDA 1972). The telechelic PIB with -NCO termini was expected and subsequently proven to be an efficient difunctional activator for CL polymerization and was the key intermediate for the synthesis of nylon-6-PIB-nylon-6 triblocks.

Experimental

All experiments and manipulations have been carried out in a stainless steel enclosure filled with nitrogen (moisture content < 50 ppm). The synthesis, purification and characterization of $HOCH_2$-PIB-CH_2OH by the inifer method has been described (KENNEDY and SMITH, 1979; KENNEDY et al. 1979; IVAN et al. 1980a). Table I summarizes synthesis conditions used and characteristics of the polyisobutylene diol starting materials prepared in this work. By careful control of experimental conditions (concentration of ingredients, nature of solvent, temperature) PIB diols in the molecular weight range from 4,000 - 69,000 have been prepared. Terminal diol functionalities were close to the theoretical value of 2.0.

The telechelic PIB diisocyanate macroactivators and nylon-6-PIB-nylon-6 triblock copolymers have been prepared as follows:

Method 1: To 2g $HOCH_2$-PIB-CH_2OH dissolved in 50 ml cyclohexane was added a solution of 5.0ml toluene-2,4-diisocyanate TDI in 50ml cyclohexane containing 0.01% di-n-butyltinlaureate catalyst (The catalyst is necessary to activate the -NCO + -CH_2OH reaction at room temperature) (-NCO/-CH_2OH = 10/1). The mixture was stirred 5-6 hours at room temperature and precipitated into a sixfold excess of dry acetone. The solvent was decanted and the polymer dried in vacuum. To remove unreacted TDI the product was redissolved in cyclohexane and reprecipitated into acetone two additional times. The dry OCN-PIB-NCO was dissolved in 50ml decalin, caprolactam was introduced, the system was heated to 105°C and ca. 0.5% (relative to CL) NaH dispersion in mineral oil (Baker) was added. After 24 hours of stirring at 105°C the product was dispersed in 300ml conc. formic acid and precipitated into 3000ml methanol. After filtering and repeated washings with methanol the crude product was dried at room temperature under vacuum for at least five days.

Method 2: A 500ml flask equipped with reflux condenser, stirrer and nitrogen inlet was charged with a solution of $HOCH_2$-PIB-CH_2OH (ca. 16g) in benzene (200ml), Method 2a; a variation of this method, Method 2b, involved the addition of 50ml decalin in select experiments. Then 150ml benzene were distilled off (azeotropic drying), an 1.5 fold molar excess TDI in 50ml benzene was added and the system refluxed for 12 hours. Subsequently caprolactam (dried under vacuum over P_2O_5 for 48 hours at room temperature) was added. The benzene was distilled off and bulk polymerization (Method 2a) or polymerization in decalin solution (Method 2b) was effected as described in Method 1. The CL polymerization phase was heterogeneous following Method 2a (bulk) and during the latter CL conversion phases by Methods 1 and 2b (decalin solution).

The crude product was extracted sequentially with n-hexane and 2,2,2-trifluoroethanol TFE. Extraction with n-hexane (good solvent for PIB, nonsolvent for PCL) removed unreacted PIB prepolymer. Infrared spectroscopy indicated the absence of C=O absorption i.e., the absence of polycaprolactam PCL in the n-hexane-soluble fraction. Thus the n-hexane-soluble fraction quantitatively reflects PIB containing species which have not been converted to block copolymers. Following _n_-hexane extraction and drying under vacuum for five days at 50°C the _n_-hexane-insoluble product was extracted with 2,2,2-trifluoroethanol, TFE, a solvent for polycaprolactam (PETIT et al. 1979) and nonsolvent for polyisobutylene. The material in the TFE-soluble fraction is essentially PCL homopolymer and the _n_-hexane-and-TFE-insoluble residue is regarded to be the target nylon-6-PIB-nylon-6 triblock. The final insoluble triblock copolymer fraction was characterized by elemental (C,H) analysis, molecular weight (osmometry in _m_-cresol at 70°C) and differential scanning calorimetry DSC (10°/min, -140 to 300°C, DuPont instrument, Model 990).

Results and Discussion

Table II summarizes synthesis conditions and results. The respective columns under Crude Products give the total weight of product obtained after extraction with methanol (assuming quantitative recovery of PIB prepolymer this weight yields total conversion, also shown), the weight of unconverted PIB prepolymer (see Experimental) obtained by extraction of the crude product with _n_-hexane, and the weight of PCL homopolymer obtained by extraction with TFE. The data under Triblock have been obtained on the _n_-hexane-and-TFE-insoluble fraction. Inspite of efforts directed toward the optimization of triblock formation the possibility that some -NCO groups in OCN-PIB-NCO remained unblocked by CL cannot be excluded. Although chemical considerations render this possibility remote, the triblock fraction may contain some PIB-nylon-6 diblocks. Characterization investigation is continuing in this direction.

Blocking efficiencies were consistently lower than 100% which may be due to several circumstances. First of all large solubility differences between PIB prepolymer and CL (particularly during the latter phases of the blocking reaction between PIB and CL) renders the mixing of the reagents difficult. Highest blocking efficiencies (B_{eff} = 40 - 60%) were obtained with the lowest molecular weight ($\bar{M}_n$ = 4,000 - 9,000) PIB macroactivators. Conceivably, increased miscibility between OCN-PIB-NCO and CL improves B_{eff}. In line with this thought higher B_{eff}'s have been obtained by the use of decalin solutions (Method 2b).

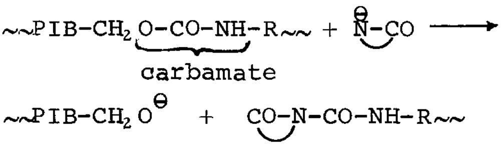
Further, rapid chain extension involving the PIB diol and TDI during macroactivator preparation may consume -NCO groups and give rise to higher molecular weight macroactivators:

$$n\ HOCH_2\text{-}PIB\text{-}CH_2OH + (2n\text{-}1)\ OCN\text{-}R\text{-}NCO \longrightarrow$$

$$OCN\text{-}R\text{-}\left[NH\text{-}CO\text{-}OCH_2\text{-}PIB\text{-}CH_2O\text{-}CO\text{-}NH\text{-}R\right]_n NCO$$

Some detailed molecular weight data, to be reported later, indicate the possible presence of this process.

The activated monomer may also attack in-chain carbamate groups and lead to chain cleavage (PETIT et al. 1979):



$$\sim\sim PIB\text{-}CH_2\underbrace{O\text{-}CO\text{-}NH}_{carbamate}\text{-}R\sim\sim + \overset{\ominus}{N}\text{-}CO \longrightarrow$$

$$\sim\sim PIB\text{-}CH_2O^{\ominus} + CO\text{-}N\text{-}CO\text{-}NH\text{-}R\sim\sim$$

The alkoxy anion may in turn start CL polymerization and thus lead to reduced blocking efficiency. To maximize triblock formation and minimize chain cleavage, the experiments were carried out under conditions similar to those used by PETIT et al. (1979) (105°C, decalin solution) who studied the cleavage of carbamates obtained of telechelic polybutadiene diols and diisocyanates.

The relatively low B_{eff}'s obtained by Method 1 may be due to moisture contamination of the macroactivator (reaction between -NCO + H_2O) during the recovery and handling of this intermediate.

The characterization of triblocks (i.e., the n-hexane-and-TFE-insoluble fraction) was rendered quite difficult on account of their insolubility in common low boiling solvents. Overall triblock composition (mole fraction of CL, X_{CL}) has been calculated from elemental analysis.

Gratifyingly, triblock molecular weights measured by osmometry and calculated from overall triblock composition in conjunction with OCN-PIB-NCO characterization data (Table I) are in excellent agreement, as shown in Table II. These results are proof positive for successful blocking, however, do not distinguish between di- and triblock formation.

Overall composition and molecular weight data yielded information as to the degree of polymerization of PCL and PIB sequences in the triblock, also shown in Table II. The molecular weight of PCL sequences can be controlled by the relative ratio of macroactivator and CL in the feed.

DSC investigations on a series of selected triblocks showed a glass transition point at -61 ± 3°C for the soft PIB segment and a melting range between 203 to 233°C for the crystalline nylon-6 segment. It seems that these values are not much affected by the relative amount of PIB and nylon-6 phases present. However, dependent on the relative composition of rubbery and crystalline sequences, a variety of elastomeric and hard thermoplastic materials have been obtained whose characterization is under way.

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TABLE I

Synthesis Conditions and Characteristics of $HOCH_2$-PIB-CH_2OH

Experimental Conditions						Results				
IB M	pDCC M	BCl_3 10^3 M	Solvent	T °C	Conversion %	$\overline{M}_n$ $x10^{-3}$	$\overline{M}_w/\overline{M}_n$	I_{eff}	F(Cl)	F(OH)
1	12.3	18	CH_3Cl	-70	87.1	4	1.60	0.99	1.97	1.95
1	4	6	CH_3Cl	-80	60.8	9	1.65	0.94	1.98	1.99
2	2	3	CH_3Cl	-80	67.2	38	1.69	0.99	1.96	1.93
2	1	1.5	CH_2Cl_2	-80	60.5	69	1.75	0.98	1.89	1.80

IB = initial concentration of isobutylene; pDCC = initial concentration of p-dicumyl chloride (inifer)

F(Cl) = chlorine functionality of Cl-PIB-Cl precursor determined by thermal dehydrochlorination (IVAN et al. 1980b)

F(OH) = hydroxyl functionality of $HOCH_2$-PIB-CH_2OH determined by differential UV spectrophotometry

I_{eff} = inifer efficiency = moles Cl-PIB-Cl formed/moles inifer used

TABLE II

Nylon-6-PIB-Nylon-6 Triblock Syntheses

Experimental Conditions				Crude Product				Triblock[c]						
Method	$HOCH_2$-PIB-CH_2OH		CL	Yield	CL	PIB[a]	PCL[b]	Yield	B_{eff}	X_{CL}	$\overline{M}_n \times 10^{-3}$		$\overline{DP}_n$	
No.	$\overline{M}_n \times 10^3$	g	g	g	conv. %	g	g	g	%		exp.	calc.	PCL	PIB
1	9	15	30	44.1	98	10.0	7.2	27.3	36	0.69	46	41	327	160
1	69	10	20	11.1	37	9.5	1.8	-	-	-	-	-	-	-
2a	4	22	41	41.0	65	11.5	2.6	27.1	41	0.44	12	10	53	71
2a	9	8	10	17.5	97	3.8	1.1	12.6	51	0.50	28	27	168	160
2a	38	16	20	21.0	58	12.0	0.9	8.1	28	0.38	67	77	256	678
2a	69	10	20	25.5	85	9.7	15.8	-	-	-	-	-	-	-
2b	4	17	30	31.5	67	6.3	2.2	23.0	55	0.36	9.8	8.6	51	71
2b	9	8	16	20.4	85	2.4	1.4	16.5	62	0.49	30	27	185	160
2b	38	15	30	31.0	69	7.3	3.3	20.3	41	0.45	126	100	725	678
2b	69	16	30	21.2	46	15	0.4	4.7	07	0.64	285	263	1911	1232

Conv. = conversion, i.e. total product after methanol extraction;

X_{CL} = mole fraction of CL in triblock determined by elemental analysis

B_{eff} = Blocking efficiency = moles triblock formed per mole prepolymer x 100

a) n-hexane soluble fraction; b) polycaprolactam: trifluoro-ethanol soluble fraction; c) n-hexane-and-trifluoroethanol insoluble fraction

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