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Polyisobutylene-containing block polymers by sequential monomer addition

IX. Poly(acenaphthylene-b-isobutylene-b-acenaphthylene)*

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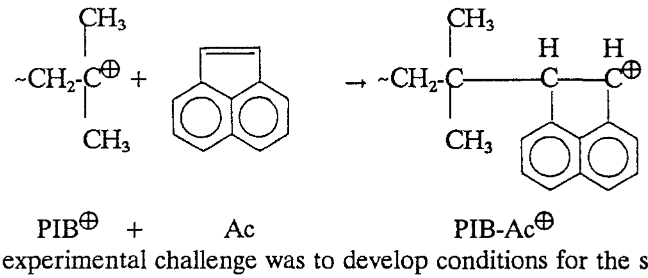
Abstract

Novel poly(acenaphtylene-b-isobutylene-b-acenaphtylene) (PAc-PIB-PAc) triblock copolymers exhibiting thermoplastic elastomer (TPE) properties have been prepared. The synthesis involved the addition of acenaphtylene (Ac) to living polyisobutylene dications ($^{\oplus}$PIB$^{\oplus}$) obtained by living isobutylene (IB) polymerization induced by the dicumyl methyl ether (DiCumOMe)/$TiCl_4$ initiating system at -80°C. The triblocks contain very short polyacenaphtylene (PAc) blocks ($M_n \approx 9{,}000$) and consequently yield very soft, low modulus TPEs. Efforts to develop conditions for the living carbocationic polymerization (LC$^{\oplus}$Pzn) of Ac have failed.

Introduction

In the course of our investigations on novel TPEs comprising a soft PIB core segment flanked by hard outer segments (1,2), we became interested in exploring the synthesis of TPEs with PAc hard segments. Incentive for this research was the very high glass transition temperature of PAc (T_g~250°C) (3). As in the previous cases (1,2), the synthetic strategy was to add the monomer which will yield the hard segment, Ac, to living $^{\oplus}$PIB$^{\oplus}$ readily prepared by techniques developed in these laboratories (2). Since Ac is known to polymerize cationically (3,4), the crossover PIB$^{\oplus}$ + Ac → PIB-Ac$^{\oplus}$ was expected to occur in view of the favorable energetics involved (the heat of Ac polymerization is 100kJ/mol (5)):



PIB$^{\oplus}$ + Ac PIB-Ac$^{\oplus}$

The experimental challenge was to develop conditions for the synthesis of triblocks with sufficiently high PAc molecular weights for TPE use. The targeted PAc-PIB-PAc exhibiting TPE properties have been prepared, however, efforts to develop living Ac polymerizations remained unsuccessful.

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Experimental

Materials

The source and purification of IB, $TiCl_4$, BCl_3, CH_3Cl, CH_2Cl_2, and methylcyclohexane (MeCH) have been described (1,2,6). Ac (Aldrich) was recrystallized twice from hexanes and sublimed in vacuo; Mp.=89°C (lit. Mp.=92°C (7)). The syntheses of 2-chloro-2,4,4-trimethylpentane (TMPCl) and 1,4-bis(2-methoxypropane)benzene (dicumylmethyl ether, DiCumOMe) have been published (8,9). 2,6-di-tert-butylpyridine (DtBP), N,N-dimethylacetamide (DMA), and 2,6-pentanedion (DPO) (all of Aldrich) were used as received. Tetra-n-butylammonium chloride (nBu_4NCl) (American Tokyo Kasei) was dried in vacuo at 50°C for 48 hrs, and cetyltrimethylammonium bromide ($CeMe_3NBr$) (Aldrich) was purified by vacuum sublimation.

Procedures, Characterization Methods

Polymerization conditions (dry box, -80°C) have been described (1,2,6). Homopolymerizations were effected in large (75 mL) culture tubes. Calculated amounts of Ac were placed into 4 mL vials (Alltech, GPC autosamplers) or beakers, and were dried in vacuo at ambient temperature for 24 h (no sublimation loss). Just before the experiment, they were rapidly placed into the entry port of the drybox, and alternatingly flushed with N_2 and evacuated. In AMI (all monomer in) experiments Ac in MeCH solutions were prepared while in IMA (incremental monomer addition) experiments stock solutions (of MeCH:MeCl 6:4) or the fine Ac powder was added. The dissolution of Ac in the charges was for all practical purposes instantaneous and the two types of additions gave similar results. Before their addition the Ac solutions or powder were cooled to the experimental temperature. The charges were quenched with prechilled MeOH and the products were poured into MeOH. The precipitated PAc was washed with MeOH to remove unreacted Ac, and was dried in vacuo.

Block copolymerizations were effected in 250 mL round bottom flasks equipped with mechanical stirrer. After IB conversion was complete (the time was determined by preliminary experiments), the Ac was added. The reaction was quenched and the product precipitated, washed, and dried. The dry copolymers were redissolved in THF and MeOH was added dropwise under vigorous stirring, until the THF:MeOH ratio reached 10:6 (v/v). These solutions which contain PAc and possibly unreacted Ac, were filtered to remove the precipitate which contained other macromolecular products (e.g., PIB). The precipitate was washed with THF:MeOH 10:6 and dried in vacuo at room temperature. Preliminary experiments showed that PAc dissolves in 10:6 THF:MeCH, however, starts to precipitate (the solution becomes hazy) upon further MeOH addition at 25°C. As the overall polarity of the products increases, that is PIB < PAc-PIB diblock < PAc-PIB-PAc triblock < PAc, only the PAc and unreacted Ac (which is soluble in THF and MeOH) remain in solution. PIB (M_n=2,500) starts to precipitate, i. e., haziness appears at 100:2 THF:MeOH.

Molecular weights were determined by osmometry and estimated by GPC. Instrumentation and general methodology have been described (6). Narrow dispersity PIB standards were used for the block copolymers, and polystyrene for PAc.

The conversion of IB and Ac, and block copolymer compositions were determined as follows: After precipitation and drying, IB conversion was calculated from the weight of the crude unwashed product. After removing unreacted Ac (washing with MeOH), Ac conversion was calculated. After fractionation with THF:MeOH 10:6, the amount of PAc homopolymer and copolymer composition could be estimated, however, this result is only approximate.

The overall composition of purified copolymers could be estimated by ^1H NMR spectroscopy and by GPC. While integration of NMR spectra in their entirety could not be carried out (see Figure 1), integration in the range from ~0.3 ppm to ~2.0 ppm gave the sum of the aliphatic protons in PIB, and in the range from ~4.0 ppm to ~9.0 ppm that of aromatic protons. Data obtained by this method were in satisfactory agreement with data obtained by other methods. UV and RI GPC traces were also used to calculate overall copolymer composition. The details of this method are described separately in an accompanying publication (10). Even when the PAc and the triblock peaks overlapped slightly, the amount of PAc in the crude product could be calculated.

Stress-strain data were obtained by ASTM D412-87 using a Monsanto Model 10 tensiometer with 2"/min (5.08cm/min) drawing rate on films cast from THF solution. The averages of 3 determinations are reported. Hardness was measured according to ASTM D2240 with a Shore A-2 durometer (average of 5 readings, 5s).

Results and Discussion

A. Attempts at Living Ac Polymerization

Orienting experiments were carried out to find conditions for living Ac polymerization. In line with past experience with IB, styrene, and styrene derivatives, we chose TMPCl as the initiator (to mimic the growing $PIB^{\oplus}$ end) and $TiCl_4$ or BCl_3 as coinitiators. Table 1 shows representative conditions used and results obtained with $TiCl_4$, and Figure 1 shows two representative ^1H NMR spectra.

Table 1: Polymerization of Ac. (0.002mol/L Ac in MeCH solution added to
a) 0.04mol/L $TiCl_4$ (control, in the absence of TMPCl), and
b) 0.002mol/L DtBP + 0.002mol/L PDO + 0.008mol/L TMPCl + 0.04mol/L $TiCl_4$; 30min; V_o=20mL)

Temperature °C	a			b		
	Conversion %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Conversion %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
MeCH:MeCl 6:4						
-30	24.7	3,600	1.55	44.6	3,300	1.44
-40	41.0	3,900	1.53	54.3	3,600	1.47
-50	48.1	4,100	1.60	63.1	3,500	1.53
-80	32.0	2,200	1.97	99.0	1,600	1.81
MeCH:MeCl 7:3						
-30	12.2	3,600	1.59	21.4	3,400	1.38
-40	28.9	3,800	1.51	36.0	3,500	1.40
-50	33.0	4,000	1.58	50.5	3,400	1.48
-80				98.5	1,680	1.76
$MeCH:CH_2Cl_2$ 47:53*						
-80				~100	1,600	1.63

*completely dissolves PAc at -80°C

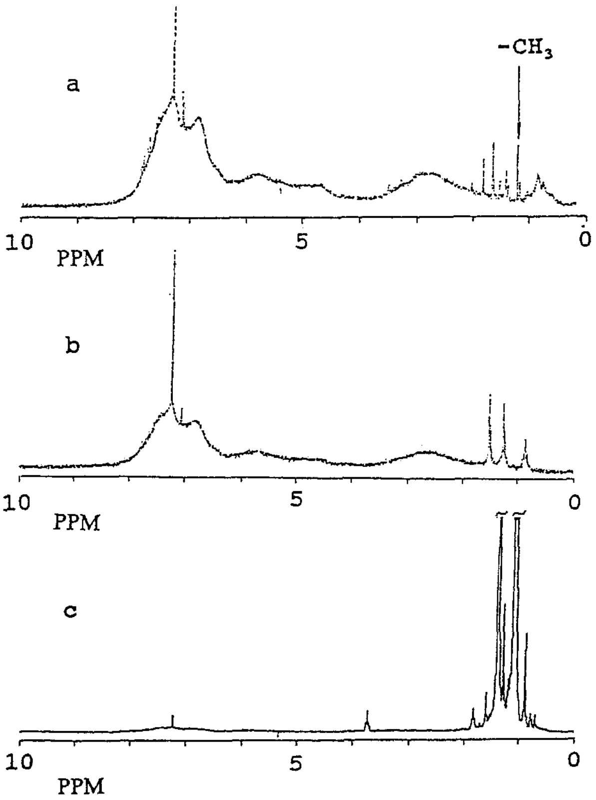

Figure 1: Proton NMR spectra of PAc. a) obtained in the presence of TMPCl; b) in the absence of TMPCl (-50°C, MeCH:MeCl 6:4, cf. Table 1); c) the triblock formed in Exp. 175.

Evidently the products prepared with the TMPCl/TiCl$_4$ initiating system after through purification exhibit the presence of CH$_3$- groups. According to this evidence the crossover from PIB$^{\oplus}$ to Ac (see formula in Introduction) has occured. However, the disappointingly low conversions indicate rapid irreversible termination; also the molecular weights are lower than expected from the [Ac]/[TMPCl] ratio and the relatively broad molecular weight distributons suggest chain transfer to monomer.

Subsequent systematic experimentation with the TMPCl/TiCl$_4$ initiating system under various conditions, that is in the -30 to -80° C range, in various solvent systems (i.e., in various mixtures of MeCl - MeCH, MeCl - hexanes, and CH$_2$Cl$_2$ - MeCH), in the presence of various concentrations of PDO, DtBP, nBu$_4$NCl, and CeMe$_3$NBr, did not yield living polymerization. Similar experiments with the TMPCl/BCl$_3$ combination did not even show evidence for -CH$_3$ group incorporation into PAc; therefore experimentation with BCl$_3$-based systems were discontinued. Thus it appears that the polymerization of Ac can be initiated in a controlled manner by the TMPCl/TiCl$_4$ system, however, the polymerization is not living. Ac polymerizations respond only marginally to the presence of additives and/or reaction conditions found to be beneficial to bring about living IB or styrene polymerizations.

B) Synthesis and characterization of PAc-PIB-PAc

The synthesis of PAc-PIB-PAc was studied by adding Ac solutions or bulk (powdery) monomer to living $^{\oplus}$PIB$^{\oplus}$ cations. Bulk Ac could be used because the dissolution of the powder was rapid (however the saturation concentration of Ac was low at -80°C). On addition of Ac solutions impurities are inevitably added to the system and the charges are diluted. The $^{\oplus}$PIB$^{\oplus}$ was prepared by the DiCumOMe/TiCl4 initiating system (1,2) and its Mn was targeted to be ~50,000 g/mole. After 2 or 3 incremental IB additions, i.e., when we were certain that the desired intermediate was on hand, and just before Ac addition a sample was withdrawn to ascertain I_{eff} (initiation efficiency: (g polymer/Mn)/mole DiCumOMe), Mn and Mw/Mn.

Table 2 shows the results of four representative experiments. Evidently the first or IB phase of the experiments were close to target. The molecular weights of the triblocks determined by osmometry were larger than those by GPC (PIB calibration) most likely because the contribution of the rigid PAc coils to the overall hydrodynamic volume of the triblock is much lower than those of the mobile PIB segments.

The compositions have been calculated from the UV and RI (GPC) traces. Similar values have been calculated from the molecular weight of PIB midsegments or from the osmometric molecular weights of triblocks.

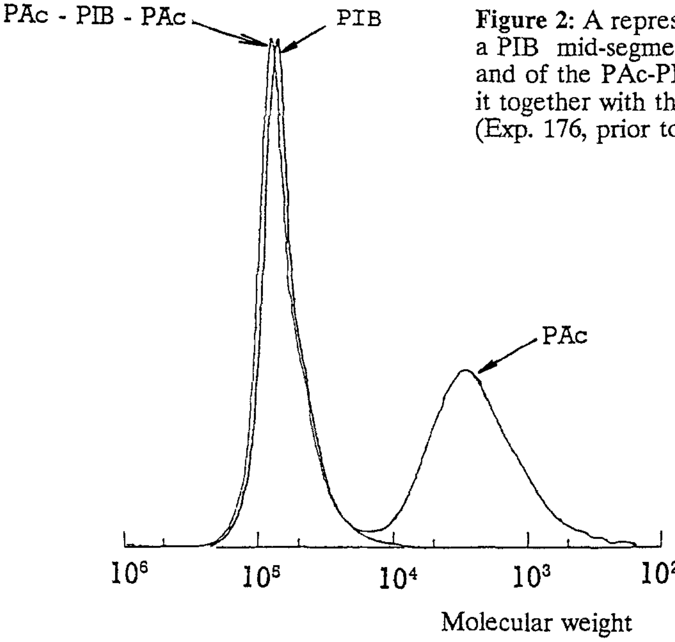

Figure 2: A representative GPC trace of a PIB mid-segment before blocking, and of the PAc-PIB-PAc formed from it together with the PAc contamination. (Exp. 176, prior to purification).

Figure 2 shows the GPC trace of a PIB mid-segment together with the crude product containing the desired PAc-PIB-PAc plus unblocked PAc. The shift in the position of the PIB peak toward higher molecular weights (lower elution counts) is small but reproducible, therefore significant; it indicates the blocking of PAc from $^{\oplus}$PIB$^{\oplus}$. The broad peak at lower molecular weights is due to unblocked PAc, it disappears after purification of the triblock. The magnitude of this peak can be used to calculate the PAc content of the crude product.

Table 2: Synthesis and properties of PAc-PIB-PAc*

Exp.		174	175	176	177
MeCH:MeCl		6:4	7:3	6:4	7:3
DiCumOMe, mol x 10^3		0.2	0.2	0.2	0.24
DMA, mol x 10^3		0.4	0.4	0.4	0.24
DtBP, mol x 10^3		0.4	0.4	0.4	0.48
$TiCl_4$, mol x 10^3		4	4	4	4.8
IB phase					
IB, mol x 100		4x4.5	4x4.5	4x4.5	4x4.5
Conversion, %		100	66.7	~100	~100
$\bar{M}_n$		58,200	38,600	53,000	57,000
$\bar{M}_w/\bar{M}_n$		1.24	1.22	1.24	1.23
Initiator efficiency, %		86	86	95	75
Ac phase					
Ac, mol x 100		6.25p	5.32p	9.36s	7.48s
Conversion, %					
Ac in homo PAc (by GPC)		72.7	43.1	50.2	37.0
Ac in block (by GPC)		14.0	18.0	10.9	12.2
Ac unreacted (gravimetry)		15.5	41.9	40.1	57.3
Block					
M_n**		66,900	47,500	61,400	66,900
$\bar{M}_n$		62,700	44,000	57,000	62,600
$\bar{M}_w/\bar{M}_n$		1.20	1.17	1.23	1.20
Ac content, wt %		13.0	18.0	13.4	13.2
Tensile strength, MPa		14.7±0.4	11.4±0.4	11.7±0.4	8.8±0.3
	***	14.1±0.4	14.1±0.4	12.3±0.3	15.4±0.4
Elongation, %		793±20	629±4	765±19	873±20
	***	710	590	630	775
Moduli, MPa					
at 100% elongation		1.77±0.08	1.31±0.08	1.77±0.08	2.22±0.10
at 200% elongation		1.45±0.08	1.01±0.04	1.49±0.08	1.86±0.09
at 300% elongation		1.18±0.07	0.78±0.02	1.22±0.07	1.56±0.09
	***	2.93	7.9	1.9	1.25
Hardness, Shore 2A		37 - 39	30 - 31	29 - 30	29 - 31
	***	40	38	30	38

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*Synthesis conditions: -80°C, V_o=100mL (after the IB addition), IB additions to MeCH:MeCl 6:4 every 15 min; to MeCH:MeCl 7:3 every 20 min; Ac addition 1 h after the last IB addition, MeOH added 10 h after Ac addition.

**Measured by osmometry

***Data obtained by redissolving, filtering, recasting and retesting the samples.

p: Ac added in fine powdery form

s: Saturated Ac solution was prepared in the indicated solvent mixture at -80° C and added to the charge

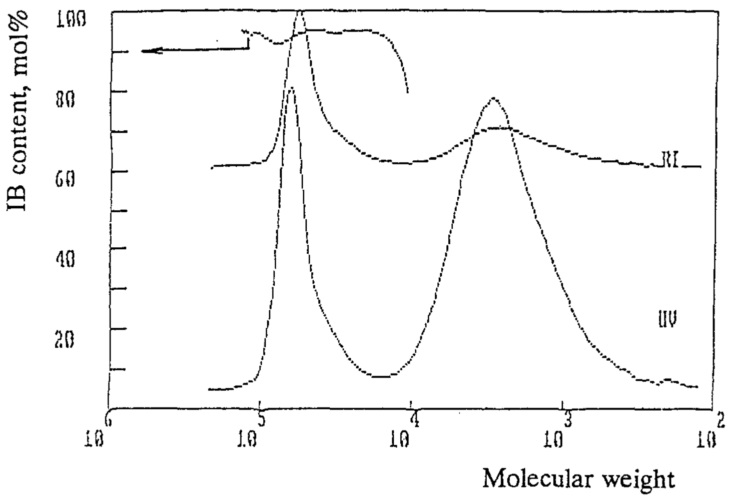

Figure 3: RI and UV traces, as a function of molecular weights of crude product and IB content (Exp. 176; PIB calibration)

Figure 3 shows the UV and RI traces and the IB content of the sample in Figure 2. The peak at high molecular weights represents the block copolymer containing 90 mole% IB. The IB content drops sharply toward the low molecular weight tail of the block copolymer peak. According to this evidence the crossover to Ac was nearly complete, at least at one end of the $^{\oplus}$PIB$^{\oplus}$. The composition of the blocks as a function of the molecular weight (elution volume) was quite similar in the other cases investigated as well. This analysis of course does not indicate whether the high molecular weight product was di- or triblock. Also, the separation of diblocks from triblocks containing very small PAc segments is a very difficult task. Circumstancial evidence that our products are in fact triblocks have been obtained by determining their mechanical properties. The results of mechanical properties of purified products are collected in Table 2 and Figure 4 shows a typical stress-strain trace.

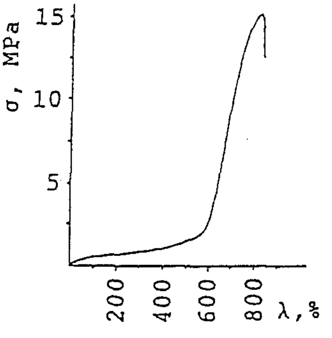

Figure 4: Stress/strain profile of a representative PAc-PIB-PAc (Exp. 174)

The good mechanical properties, particularly the high tensile strengths, indicate the presence of triblock microstructure characteristic of TPEs. Cast films were transparent and did not exhibit stress whitening even at ultimate elongation. The low moduli are due to the low amounts of PAc and the low hardness values also indicate the predominance of the rubbery PIB phase. These facts suggest a very high degree of microdomain separation. The microstructure of these TPEs are proposed be small glassy PAc segments physically crosslinking long soft PIB chains. It is truly remarkable that good TPE properties could be obtained with material containing only 13-18 wt.% hard segment (see Table 2).

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