Preparation and characterization of poly(1,4-butadiene-b-1,2-butadiene)

S. Poshyachinda, H. G. M. Edwards and A. F. Johnson*
Chemistry and Chemical Technology, Department of Chemical Engineering, University of Bradford, Bradford, West Yorkshire BD7 1DP, UK
(Received 10 November 1989; accepted 8 February 1990)

Poly(1,4-butadiene-b-1,2-butadiene) diblock polymers have been prepared anionically by sequential addition of monomer using sec-butyllithium as initiator in cyclohexane. The first block is of low vinyl units and the second block is of high vinyl units in microstructure. 1,2-Dipiperidinoethane was used as complexing agent in order to change the mode of addition of butadiene from predominantly 1,4 to 1,2 addition. The diblock polymers were characterized using Raman spectroscopy, gel permeation chromatography (g.p.c.) and dynamic mechanical thermal analysis (d.m.t.a.). The increase in molecular weight after the second batch of monomer was added is confirmed by g.p.c. Raman spectroscopy shows the difference in microstructure of the two blocks. Phase separation has been found in two diblock samples through the observation of two T_g values arising from low and high vinyl blocks.

(Keywords: anionic polymerization; diblock polymer; complexing agent; Raman spectroscopy; microstructure)

INTRODUCTION

There are many records of the fact that when butadiene is polymerized in non-polar media using an alkyllithium initiator polybutadienes of low vinyl content are produced[1]. Langer[2] found that the addition of a relatively small amount of *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TMEDA) to the butyllithium initiated polymerization of butadiene in a hydrocarbon solvent gave a product with a very high vinyl content. Halasa *et al.*[3,4] have shown that 1,2-dipiperidinoethane (DIPIP) is the most effective complexing agent for the synthesis of high-vinyl polybutadiene and the influence of DIPIP on the anionic polymerization of butadiene has been extensively studied[5,6].

Polybutadienes with a high vinyl content are of considerable technological importance. For example, Yoshioka *et al.*[7] and Odar *et al.*[8] reported that blends of *cis*-polybutadiene or *cis*-polyisoprene with high vinyl polybutadienes result in products with remarkable properties which can be compounded and vulcanized by conventional means to give passenger-car tyre materials with an excellent balance between wet-skid resistance and rolling resistance.

In this work we report the synthesis of diblock diene polymers of the general structure poly(1,4-butadiene-b-1,2-butadiene) which have a range of different block lengths in polymers which have a high overall molecular weight. The syntheses have been carried out by the sequential addition of monomer to living anionic propagating species. In all cases the first block of the polymers described comprises predominantly *cis* and *trans* microstructures, whereas the second block is of high vinyl units. The diblock polymers have many properties similar to those reported for blends of high *cis* and high *trans* polymers and the block polymer synthesis might provide a convenient route to a technically useful product without the need to indulge in the blending of thermodynamically incompatible homopolymers. The microstructures of the diblock polymers of low and high vinyl polybutadienes are characterized using Raman spectroscopy following a method suggested by Cornell and Koenig[9]. Particular attention is given to the influence of copolymer composition and molecular weight on the dynamic mechanical properties of these novel block copolymers.

EXPERIMENTAL

The preparation of the polymers was carried out using well established high vacuum techniques[10] using sec-butyllithium (Aldrich) as initiator to ensure rapid initiation rates in the hydrocarbon solvent used. Both the 1,3-butadiene monomer (Aldrich) and cyclohexane (Aldrich, h.p.l.c. grade) were purged with and distilled off n-butyllithium *in vacuo* before use. The 1,2-dipiperidinoethane (DIPIP) (Aldrich), was dried over CaH_2 under vacuum for at least two weeks before use.

The polymerization of butadiene to give a polymer with a low-vinyl content was effected in cyclohexane with sec-butyllithium as initiator at room temperature in the absence of complexing agent. In order to obtain high vinyl polybutadienes, polymerization was carried out in a similar manner but with DIPIP complexed with the living polybutadienyllithium chain ends, to give predominantly 1,2 addition of monomer to the growing chains. It has been claimed that DIPIP[3,4] is a most effective complexing agent for the production of polymers with a high 1,2 vinyl content even when present in the polymerization medium in relatively small amounts compared with initiator i.e. at low values of r where r is the concentration of DIPIP to alkyllithium initiator ($r = [\mathrm{DIPIP}]/[\mathrm{Li}]$). In this work $r = 4$ in all experiments. The preparation of the diblock polymers was effected by polymerizing the first block in cyclohexane. After the first batch of monomer had been completely polymerized, about 5 ml of the solution of living polyanions was taken

---

* To whom correspondence should be addressed

0032-3861/91/0200334-04

from the system for subsequent determination of the molecular weight and composition of the first block, and to the remainder of the reaction mixture was added an appropriate quantity of DIPIP, followed by a quantitative amount of butadiene. The reactions were carried out at 0°C in order to minimize the temperature rise resulting from the heat of reaction because polymerization is very fast in the presence of DIPIP[5]. The block length in the final products is controlled by the amount of monomer used in each batch reaction. The u.v. absorption maximum of the polybutadienyl anion at 275 nm and that at 325 nm for the species when complexed with DIPIP was measured in order to assess the concentration of living polyanions. The change in the absorption spectrum with the addition of DIPIP was measured also.

Raman spectra of the diblock polymers and the polybutadiene first stage polymer were obtained using a Spectra-Physics 2020/5 argon ion laser, with a nominal output power of 1.5 W at 488.0 nm, and a Spex Industries 1401 double monochromator with photon counting detection and reciprocal linear dispersion of 21.5 $\mathrm{cm^{-1}\,mm^{-1}}$ in the first order at 488.0 nm. Spectral slit widths of 4 $\mathrm{cm^{-1}}$ were employed and wave number calibration effected using the emission lines of a neon lamp; wave number shifts of observed Raman lines are correct to $\pm 1\ \mathrm{cm^{-1}}$.

Spectrometer control was carried out using a Nicolet 1180 computer, which facilitated multiple scanning of spectral ranges and improved signal-to-noise ratios over those of single-scan spectra. A standard curve analysis programme package enabled curve resolution and band area measurements to be made over defined wavenumber units and this was important for the quantitative aspects of this work.

Molecular weight determination and molecular weight distribution measurements were made using a Waters Associates gel permeation chromatograph fitted with a Model R410 refractometer detector using chloroform as the eluant. Two PL Gel columns were used (Polymer Laboratories Ltd), one 10^3 Å pore size and one 10^5 Å in pore size, both with 10 μm bead diameter. Approximately 100 μl of polymer solution (0.25 wt% concentration) were injected into the columns and analyses carried out with eluant flow rates of 1 ml $\mathrm{min^{-1}}$. The columns were calibrated with polystyrene standards, hence, the molecular weights quoted in this work are polystyrene equivalents. The raw data were collected and processed and data reduction was by means of a software package developed in our own laboratories[11].

The dynamic mechanical behaviour of the polymers was studied using a Polymer Laboratories dynamic mechanical thermal analyser (DMTA Mark II). The frequency and heating rates used were 1 Hz and 3°C $\mathrm{min^{-1}}$, respectively. The polymers were prepared for analysis by casting films from cyclohexane solutions of the polymers. These were then cut into rectangular shapes for shear-head configuration of the instrument.

RESULTS AND DISCUSSION

The molecular weights of the polymers are shown in *Table 1*. The peak molecular weight was used for the calculation of molecular weight of the two blocks because the molecular weight distributions of the three diblocks are not unimodal, as shown in *Figure 1*, due to the killing of some living chain ends arising from impurities present in the second batch of monomer. G.p.c. results show the increase in molecular weight after the second batch of monomer was added into the living solution. This second batch of monomer underwent 1,2 addition. Complexing agents complex the living chain ends and affect the charge distribution to the γ-carbon atoms of the allylic chain ends which then favours the 1,2 mode of addition[6]. In the case of DIPIP, it has been suggested that the steric hindrance of the DIPIP molecule causes change in the mode of addition of the monomer[3]. DIPIP also causes the active centres to be largely in the *trans* form[6]. The shift in u.v. absorption of polybutadienyllithium when complexed with DIPIP demonstrates the formation of this complex, similar to the results reported by Bywater *et al.*[5].

Raman spectroscopy was used to monitor changes in polymer microstructures produced by different polymerization routes. In the ν(C=C) stretching region of the Raman spectrum of the polybutadienes, $\Delta\tilde{\nu} = 1540$–$1740\ \mathrm{cm^{-1}}$, the ν(C=C) stretch of the (1,2)-vinyl, (1,4)-*cis* and (1,4)-*trans* species occur at $\Delta\tilde{\nu} = 1640$, 1650 and 1664 $\mathrm{cm^{-1}}$, respectively. The total band area in the

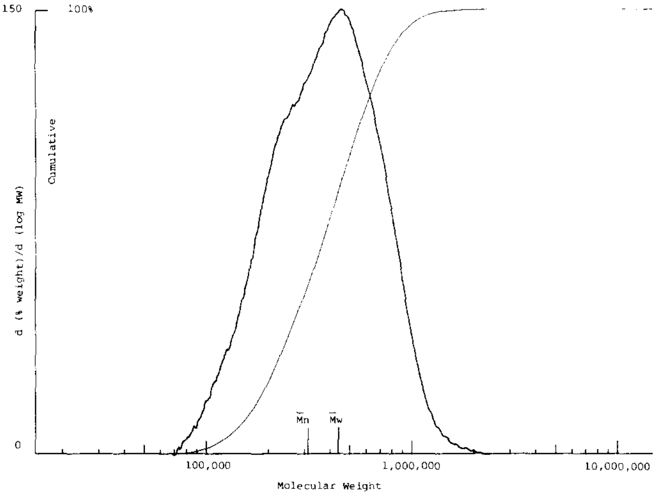

Figure 1 Molecular weight distribution of PBB-25/75

Table 1 Molecular weight and polydispersity of poly(1,4-butadiene-b-1,2-butadiene)

Sample	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	M_{p_1}[a]	M_{p_2}[b]
PBB-0/100	172 000	155 000	1.11	—	167 000
PBB-25/75	438 000	313 000	1.40	128 000	340 000
PBB-50/50	479 000	334 000	1.43	209 000	204 000
PBB-75/25	385 000	278 000	1.39	279 000	34 000
PBB-100/0	534 000	345 000	1.55	413 000	—

[a] M_{p_1} = peak molecular weight of the first block
[b] M_{p_2} = peak molecular weight of the second block

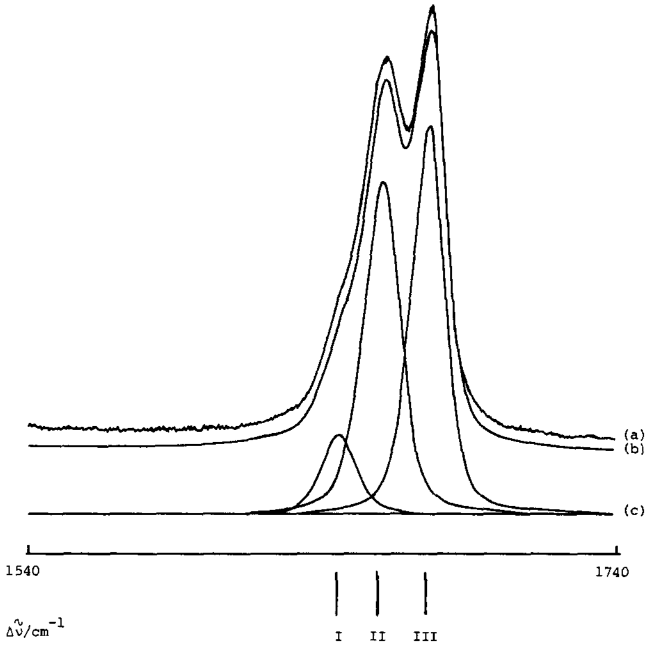

Figure 2 Raman spectrum of first stage polymerization of butadiene, $\Delta\tilde{\nu} = 1540\text{–}1740\ \mathrm{cm}^{-1}$; curve (a) observed spectrum; curve (b) computer calculated; curve (c) resolved spectrum; I (1,2)-vinyl, II (1.4)-*cis*, III (1,4)-*trans* polybutadiene. Calculated composition: I (9.6%), II (43.8%) and III (46.6%)

ν(C=C) stretching region is representative of the total (C=C) content in the polymeric material. The linear dependence of band intensity (area) with concentration of the species gives, in addition, a good sensitivity of detection and measurement of each of the ν(C=C) bands which arise from the three microstructures given above.

The Raman spectrum of the first stage polymerized polybutadiene in the wave number shift region, $\Delta\tilde{\nu} = 1540\text{–}1740\ \mathrm{cm}^{-1}$, is given in *Figure 2* with the computer-fitted spectrum and the spectrum resolved into three bands arising from the (1,2)-vinyl, (1,4)-*cis* and (1,4)-*trans* polybutadiene components.

In *Figure 3* is shown a composite of the spectral regions, $\Delta\tilde{\nu} = 1540\text{–}1740\ \mathrm{cm}^{-1}$, for five compositions of PBB series in the range 100/0 to 0/100. The (1,2)-vinyl, *cis* and *trans* content of each diblock polymer obtained from their spectra are shown in *Table 2*. The accuracy of the determination of microstructure composition is about ±1%. In each case, three spectral scans over the wave number region were accumulated and the raw data processed to give the composition results. The total time taken to record each spectrum was approximately 10 min.

The results of the DMTA measurements are shown in *Figures 4* and *5*. The plots of log tan δ and log G' against temperature in the range −100°C to 50°C show that phase separation occurs for PBB-50/50 and PBB-75/25. The two glass transitions corresponding to the T_g values of low and high vinyl blocks can be seen. The damping factor at the T_g of PBB-100/0 is lower than that of the PBB-0/100 sample. For PBB-100/0 T_g appears at −72°C whereas that of PBB-0/100 is at 12°C. The high T_g in PBB-0/100 as compared with PBB-100/0 is due to the vinyl group restricting the movement of the backbone, whereas *cis*- and *trans*-microstructures have no pendant group which makes the main chain more flexible. PBB-50/50 and PBB-75/25 show two T_g values at −72°C and 12°C. The increase in the damping factor of

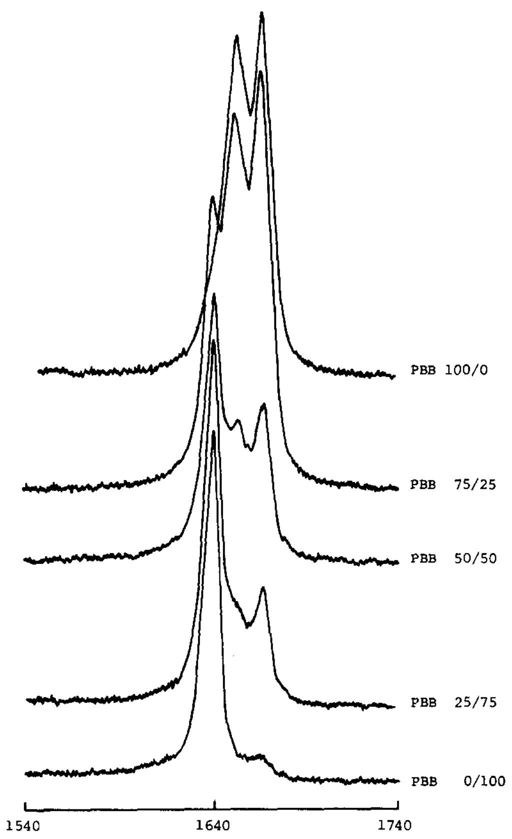

Figure 3 Microstructure determination of diblock polybutadienes; Raman spectra, $\Delta\tilde{\nu} = 1540\text{–}1740\ \mathrm{cm}^{-1}$ for PBB-100/0, 75/25, 50/50, 25/75 and 0/100 compositions

Table 2 Percentage microstructure of the diblock polymers

	First block			Second block		
Sample	vinyl	*cis*	*trans*	vinyl	*cis*	*trans*
PBB-0/100	—	—	—	94.2	0.0	5.8
PBB-25/75	9.6	43.8	46.6	94.0	0.4	5.6
PBB-50/50	9.5	43.3	47.2	94.1	0.0	5.9
PBB-75/25	9.3	44.3	46.4	94.4	0.2	5.4
PBB-100/0	9.9	43.5	46.4	—	—	—

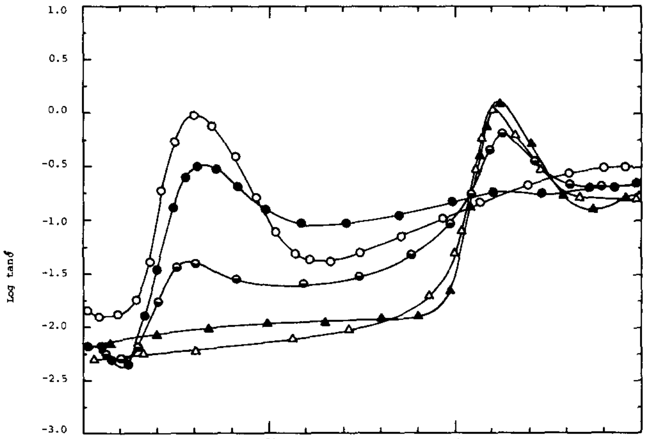

Figure 4 Temperature dependence of log tan δ for poly(1,4-butadiene-b-1,2-butadiene); ○ PBB-0/100; ● PBB-25/75; ◒ PBB-50/50; △ PBB-75/25; ▲ PBB-100/0

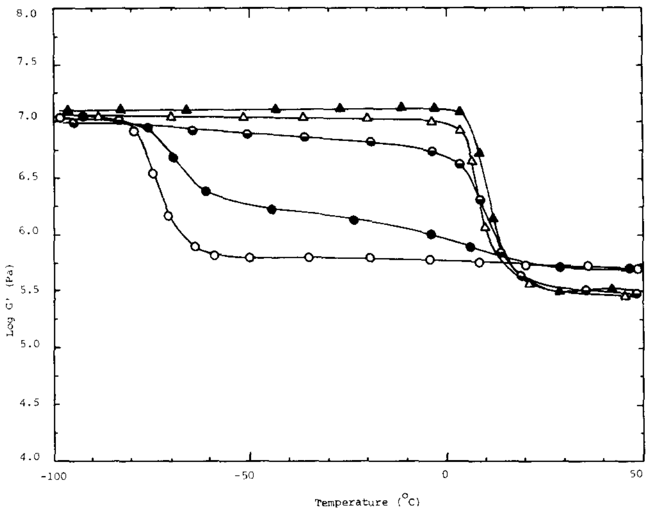

Figure 5 Temperature dependence of log G' for poly(1,4-butadiene-b-1,2-butadiene); ○ PBB-0/100; ● PBB-25/75; ◓ PBB-50/50; △ PBB-75/25; ▲ PBB-100/0

PBB-100/0 after the T_g is due to sample expansion. The same effect can be seen in PBB-75/25 which contains longer 1,4 block length than 1,2. The sample expansion results in the T_g of the high-vinyl block being obscured. In contrast, PBB-25/75 shows a single T_g at 10°C which is 2°C lower than that of the high vinyl block. This is thought to be due to the compatibility of the two blocks at this size of block length. However, the degree of compatibility must depend not only on the block length but also on the molecular weight of the entire chain. Further experiments are required to determine precisely which combination of block length results in phase separation because the data obtained here are from only three block lengths.

Figure 5 shows the dependence of log G' on temperature. PBB-0/100 and PBB-25/75 exhibit a decrease in log G' above 0°C, corresponding to their T_g values. PBB-100/0 also reveals a major decrease in the log G' value at temperatures above -70°C, again due to its T_g. In contrast, PBB-50/50 and PBB-75/25 show two decreases in log G' below -70°C and above 0°C, due to the two transitions arising from the low and high vinyl blocks, respectively.

ACKNOWLEDGEMENT

We thank the Institute for the Promotion of Teaching Science and Technology, Thailand, for a research studentship to S. Poshyachinda.

REFERENCES

1 Morton, M. 'Anionic Polymerization, Principle and Practice', Academic Press, New York (1983)
2 Langer, A. W. Jr., *Am. Chem. Soc. Div. Polym. Prepr. No. 1* 1966, 7, 132
3 Halasa, A. F., Lohr, D. F. and Hall, J. E. *J. Polym. Sci., Polym. Chem. Edn* 1981, **19**, 1357
4 Halasa, A. F., Schulz, D. N., Tate, D. P. and Mochel, V. D. *Adv. Organomet. Chem.* 1980, **18**, 55
5 Bywater, S., McKerron, D. H., Worsfold, D. J. and Schué, F. *J. Polym. Sci., Polym. Chem. Edn* 1985, **23**, 1997
6 Bywater, S. and Worsfold, D. J., in 'Advances in Elastomers and Rubber Elasticity', (Eds J. Lal and J. E. Mark), Plenum Press, New York (1986)
7 Yoshioka, A., Komuro, K., Ueda, A., Watanabe, H., Akita, S., Masuda, T. and Nakajima, A. *Pure and Appl. Chem.* 1986, **58**, 1697
8 Odar, J. and Von Hellens, W. US Patent 4721 749 (1988)
9 Cornell, S. W. and Koenig, J. L. *Macromolecules* 1969, **2**, 540
10 Fetters, L. J. *J. Res. Nat. Bur. Stan.* 1966, **70A**, 421
11 Gosden, R. G., University of Bradford, available through Aston Scientific Ltd., Clinton, Bucks., UK