

SYNTHESIS AND CHARACTERIZATION OF COMB-SHAPED POLYBUTADIENES*

MA Jingjing (马京晶), HOU Yafen (侯雅芬)**

and HUANG Baotong (黄葆同)

(Changchun Institute of Applied Chemistry, Academia Sinica, Changchun)

ABSTRACT

Polybutadiene (PB) was chlorinated with $t\text{-BuOCl}$ without chain crosslinking and degradation to give chlorinated polybutadiene (Cl—PB) with active allylic chlorine atoms on the backbone. Comb-shaped PB was prepared by coupling of Cl—PB with "living" PB anions in a mixed solvent of cyclohexane and tetrahydrofuran. Characterization by GPC and osmometry showed that purified products were well-defined comb-shaped PB composed of low polydispersity backbone chain and randomly distributed grafts of uniform length. The average number of branches could be varied in a wide range to meet the needs of structure-properties relationship studies.

INTRODUCTION

A comb-shaped polymer is composed of a linear backbone and random grafts of known and usually constant length, backbone and grafts being of the same chemical constitution. In recent years studies on structure-properties relationship aroused intensive interest in the syntheses of comb-shaped polymers as tailor-made model macromolecules.

Graft copolymers can be prepared by (1) grafting-from, (2) grafting-onto, or (3) macromer copolymerization^[1] processes. The grafting-onto method has been used in the synthesis of most comb-shaped polystyrenes^[2].

As reported in the literature^[3], preparation of branched polybutadienes (PB) by grafting-from process always resulted in degradation and crosslinking of the backbone during its metalation and gave polymers with uncontrolled, polydispersed grafts. This work undertook to synthesize comb-shaped PB by grafting-onto method. In the process, PB was first chlorinated with *tert*-butyl hypochlorite ($t\text{-BuOCl}$) to give chlorinated PB (Cl—PB) with introduction of active allylic chlorine atoms on the backbone chain, and then the comb-shaped PB with randomly distributed grafts was formed by nucleophilic attack of "living" PB anions (PB^-) on Cl—PB. The merits of this method are: (1) the final product is a well-defined polymer, since the backbone and grafts can be characterized independently before the coupling reaction, and (2) monodispersity of the comb-shaped polymer, especially that in the length of the grafts, is better than those obtained by other processes.

EXPERIMENTAL

1. Materials

Cyclohexane and *n*-hexane (both chemical pure grade) were dried over 4A molecular

* Received September 16, 1984.

** Thesis student of the Dalian Institute of Technology, 1982

sieves and purged with purified argon stream. Tetrahydrofuran (THF) was distilled under argon atmosphere in the presence of *n*-butyl lithium (*n*-BuLi) and the middle fraction was taken for use. Butadiene (polymerization grade, 99% purity) was dried over alumina and freshly distilled before polymerization. The preparation of *n*-BuLi benzene solution has been described^[11]. *t*-BuOCl was prepared according to literature^[41].

2. *Synthesis and chlorination of PB*

PB for both the backbone and the grafts was obtained separately by polymerization of butadiene in hexane under argon atmosphere using *n*-BuLi as catalyst^[5]. For chlorination of PB at ambient temperature, see [6].

3. *Coupling reaction and product purification*

After "living" PB for grafts had been pre-polymerized, the solution of Cl—PB in THF was added into the reaction vessel. After shaking thoroughly, the reactor was put in a thermostat for a specified time. A small amount of methanol was added to terminate the reaction and the product was precipitated in an excess of methanol. The polymer was dried and its toluene solution (%) was selectively fractionated with methanol to remove uncoupled PB.

4. *Polymer characterization*

Number-average molecular weight ($\bar{M}_n$) of the polymer was measured in toluene (37°C) using a Knauer Membrane Osmometer. Molecular weight distribution (MWD) data were obtained on a GPC column. Chain micro-structure of PB was determined with a Perkin-Elmer 599 IR spectrometer (CS₂ solution). Chlorine content was determined by combustion method^[7].

RESULTS AND DISCUSSION

1. *Chlorination of PB*

Under ultra-violet light, *t*-BuOCl decomposes into *t*-BuO • radicals^[8], which predominantly abstract allylic hydrogen atoms rather than act on double bonds of PB, thus giving rise to thermodynamically more stable allylic structures. Allylic chlorine introduced into backbone in this manner had been used successfully to act as potential centers for cationic graft polymerization from PB^[6].

Studies on chlorination conditions revealed that chlorine content of Cl—PB increased with dosage of *t*-BuOCl (Fig. 1) but did not change remarkably when UV irradiation time was prolonged from 15 to 170 minutes (Fig. 2). This infers that under our experimental conditions short time irradiation was enough to make *t*-BuOCl decompose into *t*-BuO • radicals and prolonged irradiation was unnecessary for chlorination of PB.

As pointed out earlier, degradation and crosslinking of PB chains always occurred when active centers were introduced into polymer chains by metallation. This would strongly hamper the preparation of well-characterizable comb-shaped PB structures. To examine the effect of chlorination with *t*-BuOCl on the structure of PB backbone chain, GPC curves were

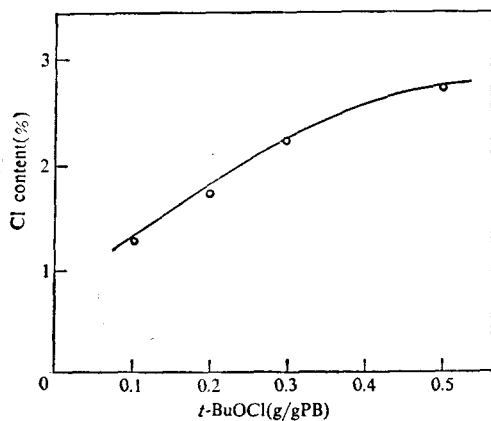


Fig. 1 Effect of t -BuOCl dosage on chlorine content of Cl-PB
[PB] = 2g/100 ml hexane; UV irradiation time 60 min

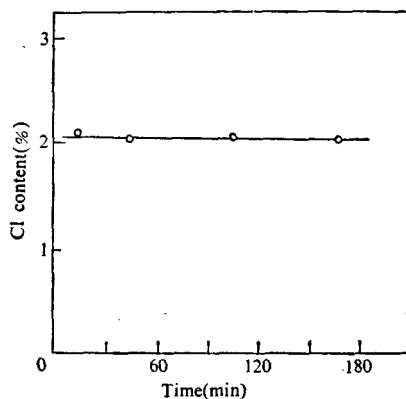


Fig. 2 Effect of UV irradiation on chlorine content of Cl-PB
[PB] = 2g/100 ml hexane; t -BuOCl 0.3 g/g rubber

run on PB before and after chlorination (Fig. 3). Nearly the same profile of the two curves illustrates that no obvious degradation and crosslinking occurred during chlorination. IR analysis of the samples proved that there was no detectable variation in chain micro-structure of PB after chlorination.

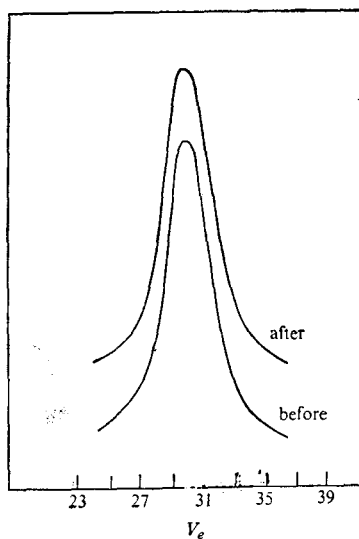


Fig. 3 GPC curves of PB before and after chlorination

2. Factors affecting coupling reaction

(1) Reaction temperature

There are two different views on the effect of temperature on coupling reaction between poly(chloromethylstyrene) (PCMS) and "living" PS anions (PS^-). Takaki^[9] and Candau^[10]

suggested that high coupling efficiency could be achieved at low temperatures because side reactions were suppressed. Ishizu^[11] reported, however, an increase in extent of coupling at fairly elevated temperatures.

Coupling reaction of Cl—PB with PB⁻ was carried out at -40, 0, and 50°C, respectively (Table 1). Results showed that higher coupling efficiency was obtained at lower temperatures. Obviously, our result is in fairly good agreement with the temperature dependency reported by Takaki and coworkers^[9]. Nevertheless, we observed that the product obtained at higher temperatures sometimes contained very small amount of micro-gel, which might have been resulted from metal-halide exchange reaction^[12] at the higher temperature.

Table 1 Dependence of coupling reaction on temperature*

Sample	$\bar{M}_{n,b}^{(1)}$ $\times 10^{-4}$	$\bar{M}_{n,g}^{(2)}$ $\times 10^{-4}$	[PB ⁻]/[Cl] ⁽³⁾ (mole/mole)	Temp. (°C)	$\bar{N}_g^{(4)}$	GE ⁽⁵⁾ (%)	$[\eta]$ (dl/g)
CT1	19.0	4.9	0.56	-40	118	91	5.59
CT2	19.0	4.5	0.61	0	61	47	4.66
CT4	19.0	5.2	0.53	50	54	42	4.21

* Reaction time 96 hours.

1) $\bar{M}_{n,b}$, $\bar{M}_n$ of the backbone; 2) $\bar{M}_{n,g}$, $\bar{M}_n$ of the grafts;

3) [Cl], concentration of chlorine atoms on Cl—PB;

4) $\bar{N}_g$, average number of branches per molecule;

5) GE, grafting efficiency based on Cl content,

$$GE = \frac{\bar{N}_g}{\text{av. no. Cl atoms on backbone chain}} \times 100.$$

(2) [PB⁻]/[Cl] ratio

Results of coupling reaction at various [PB⁻]/[Cl] ratio, where [PB⁻] and [Cl] are concentrations of polybutadiene anion and chlorine atom (in mole) respectively, showed that $[\eta]$ and the average number of grafts, $\bar{N}_g$, of the products increased with [PB⁻]/[Cl] ratio (Table 2). Increase in grafting efficiency at higher [PB⁻]/[Cl] ratios resulted from higher collision probability of "living" anions with the active centers on the backbone. However, it should be pointed out that too high a [PB⁻]/[Cl] ratio for the coupling reaction is not recommended, since larger amount of "living" anions usually incite side reactions much more easily.

Table 2 Effect of [PB⁻]/[Cl] ratio on coupling reaction*

Sample	$\bar{M}_{n,b}$ $\times 10^{-4}$	$\bar{M}_{n,g}$ $\times 10^{-4}$	[PB ⁻]/[Cl] (mole / mole)	$\bar{N}_g$	Ct (%)	$[\eta]$ (dl/g)
CC1	19.0	5.2	0.42	24	18	4.26
CC2	19.0	4.9	0.70	38	29	5.23
CC3	19.0	5.6	1.40	* 123	94	5.87

* Reaction time 96 hours, temperature 50°C

(3) Solvent polarity

Our previous work^[18] has shown that addition of THF could drastically increase coupling.

efficiency. The mechanism on which polar solvent affects the coupling react should be the same as that in anionic polymerization.

It is generally accepted that in anionic polymerization the activity of "living" terminals decreases in the order: free ion $>$ loose ion $>$ contact ion pair. Addition of polar solvent increases the concentration of free ions and loose ion pairs, resulting in an enhancement of polymerization rate.

The same effect occurred in coupling reaction. By addition of THF, Li^+PB^- pairs are highly solvated to form loose ion pairs or free ions. Then it would be much easier for PB^- in the form of a free ion or a loose ion pair to make a nucleophilic attack on the allylic carbon atom. In addition, THF is a good solvent for most of polymers that makes PB macromolecular coils more extended, so there would be more chance for an active group on the backbone to couple with PB^- anions.

Our investigation on coupling reaction conditions showed that reaction parameters, such as temperature, active group ratio and solvent polarity, had profound effect on Cl-PB/PB^- coupling reaction. The similarity between regularities governing Cl-PB/PB^- and PCMS/PS^- coupling reactions indicates that these two coupling reactions follow nearly the same mechanism.

3. Polymer characterization

(1) Product isolation

As shown in Fig. 4, characteristic GPC peaks of comb-shaped PB and graft PB which is

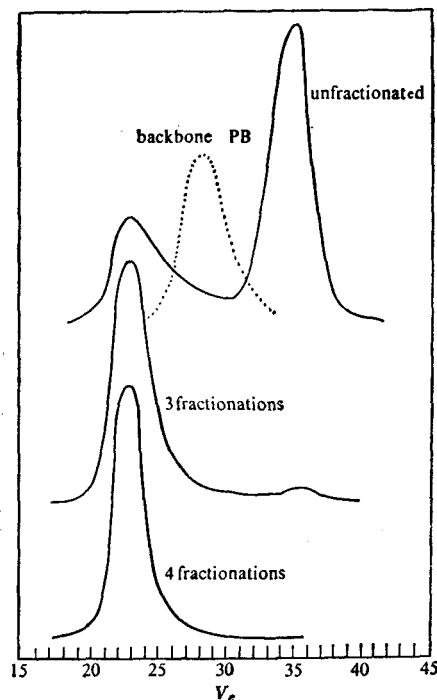


Fig. 4 GPC profiles of samples before and after precipitation fractionation

much smaller in molecular weight do not overlap. Fractionation by selective precipitation was used to remove uncoupled PB. After four successive fractionations, pure comb-shaped PB was obtained, as evidenced by the disappearance of the characteristic peak of graft PB on GPC profile.

(2) Characterization of comb-shaped PB

Characterization of the starting backbone PB and of the graft PB (Table 3) demonstrates that both of these are mono-dispersed PB and are of nearly the same chain micro-structure.

Table 3 Characterization of starting backbone PB and graft PB

Sample	$\bar{M}_w^{(1)}$ $\times 10^{-4}$	$\bar{M}_n^{(1)}$ $\times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	Micro-structure (%)		
				cis-1,4	trans-1,4	1,2
			Backbone			
P2	25.6	20.0	1.28	44.0	48.8	6.9
P10	33.4	27.6	1.21	49.0	43.6	7.4
P5	90.8	74.4	1.22	56.9	35.7	7.4
			Graft			
B1	5.3	4.5	1.18	50.0	40.1	9.9
B2	6.0	4.8	1.25	51.6	39.4	9.0
B3	5.7	5.2	1.10	—	—	—
B4	6.0	5.6	1.06	—	—	—
B5	6.7	5.8	1.15	41.7	48.5	9.8

1) By GPC method.

As the structure of the backbone and the graft PB had been characterized separately before coupling, the molecular structural parameters of the comb-shaped PB could easily be calculated according to the following equations, provided that molecular weight of comb-shaped PB had also been determined:

$$\bar{N}_g = (\bar{M}_{n,g} - \bar{M}_{n,b}) / \bar{M}_{n,g} \quad (1)$$

$$\bar{M}_{n,bb} = \bar{M}_{n,b} / \bar{N}_g \quad (2)$$

where $\bar{N}_g$ is the average number of branches per molecule, and $\bar{M}_{n,bb}$ the number average molecular weight of segments between neighboring branching points on the backbone.

Characterization of some of the samples of comb-shaped PB is listed in Table 4. From the results we come to the conclusion that comb-shaped PB with well-defined molecular structure could be conveniently obtained by coupling reaction between a backbone PB and chosen graft PB of proper molecular weight. Graft copolymers with much larger $\bar{N}_g$ and higher GE, e. g., N_g up to 118 and GE up to 91%, can be obtained though the accuracy is questionable due to too high MW in their determination.

Table 4 Molecular structure of comb-shaped PB

Sample	$\bar{M}_{n,c}^{(1)}$ $\times 10^{-4}$	$\bar{M}_{n,b}^{(1)}$ $\times 10^{-4}$	$\bar{M}_{n,g}^{(2)}$ $\times 10^{-4}$	$\bar{N}_g$	$\bar{M}_{n,bb}$ $\times 10^{-3}$	GE (%)	$[\eta]$ (dl/g)
C1	65.8	48.3	2.2	8	6.0	4	—
C2	76.7	48.3	2.9	10	4.8	7	—
C3	78.0	24.1	2.9	19	1.3	11	—
C4	83.0	21.3	4.5	14	1.5	23	—

1) By osmometry. 2) By GPC method.

It is generally accepted⁽¹⁴⁾ that the coupling reaction of "living" polymer anions with a backbone polymer occurs statistically and that fluctuation in composition within a sample can be neglected. The MWD of the copolymer is determined only by that of the backbone chain. The anionically polymerized backbone PB used in our experiment had narrow MWD. Therefore, the MWD of the comb-shaped PB obtained by the grafting-onto method should be superior to that of the products prepared by commonly used grafting-from processes. This is visibly supported by the sharp peak of GPC curves of the backbone Cl-PB and the comb-shaped PB (Fig. 5).

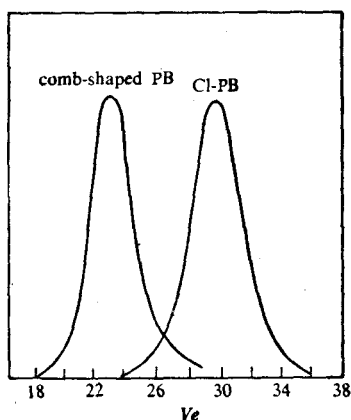


Fig. 5 GPC curves of backbone Cl-PB and comb-shaped PB

Acknowledgement The authors wish to thank Ms. Chen Baokuen for providing analysis data and Ms. Hu Huizhen and Ms. Yu Min for helping with osmometry and GPC measurements.

REFERENCES

- [1] 马京晶、庞德仁、黄葆同, 高分子通讯, **1984**, 161
- [2] Pannell, J., *Polymer*, **1971**, *12*, 558.
- [3] Tate, D.P., Halasa, A.F., Webb, F.J., Koch, R.W., Oberster, A.E., *J. Polymer Sci.*, A-1, **1971**, *9*, 139.
- [4] Teeter, H.M., Bell, E.W., "Organic Syntheses", Coll. Vol. IV, Ed. Rabjohn, N., John Wiley & Sons, New York, **1963**, p. 125.
- [5] Hsieh, H.L., *J. Polymer Sci.*, **1965**, A3, 153.
- [6] Ambrose, R.J., Newell, J.J., *J. Polymer Sci., Polym. Chem. Ed.*, **1979**, *17*, 2129.
- [7] Cook, W.A., *Microchem. J.*, **1961**, *5*, 67.
- [8] Poutsma, M.L., "Free Radicals", Vol. II, Ed. Kochi, J.K., John Wiley & Sons, New York, **1973**, p. 159.
- [9] Takaki, M., Asami, R., Ichikawa, M., *Macromolecules*, **1977**, *10*, 850.
- [10] Candau, F., Franta, E., *Makromol. Chem.*, **1971**, *149*, 41.
- [11] Ishizu, K., Fukutomi, T., Kakurai, T., *Polymer J.*, **1975**, *7*, 228.
- [12] Altares, Jr. T., Wyman, D.P., Allen, V.R., Meyersen, K., *J. Polymer Sci.*, **1965**, A3, 4131.
- [13] 马京晶, 长春应用化学研究所硕士论文, **1981**.
- [14] Rempp, P., Franta, E., Herz, J., *Polym. Prepr.*, **1980**, 21(1), 28.