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Synthesis of New Graft Polymers *via* Anionic Grafting of β-Butyrolactone on Poly(methyl methacrylate)

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ABSTRACT: Novel graft polymers have been synthesized *via* an anionic grafting reaction of β-butyrolactone (β-BL) on poly(methyl methacrylate) (PMMA). It was found that partially saponified PMMA bearing carboxylate anions complexed by 18-crown-6 potassium counterion acts as a macroinitiator of β-butyrolactone polymerization. As a result, graft polymers of PMMA with grafted poly(butyrolactone) side chains are produced in high yield over a wide graft composition range.

Introduction

Anionic polymerization of racemic β-butyrolactone (β-BL) leads to a biodegradable amorphous polyester.[1-3] Several block polymers and macromonomers of β-BL have been obtained using supramolecular complexes of alkali metals or alkali-metal naphthalenides as homogeneous anionic initiators.[4-6]

On the other hand, poly(methyl methacrylate) is a versatile polymeric material with many applications also in surface coating industries.[7]

Grafting is considered an important technique for modifying physical and chemical properties of polymers. Several graft polymers of polyacrylates have been recently developed for specific applications such as in coatings, as surface modifiers, and as surface-tension agents and thermoplastic elastomers.[8-10]

The introduction of biodegradable segments into acrylate backbones, which are nontoxic and which do not undergo eutrophication, should enable the polyacrylate modification directed toward biodisintegrable polymers possessing possible applications in medicine and environment protection.[11]

The synthesis of new graft polymers *via* anionic grafting of β-butyrolactone on poly(methyl methacrylate) is presented in this paper. Their composition and the average length of poly(β-butyrolactone) segments were estimated.

Experimental Section

Materials. β-Butyrolactone [Fluka; bp 47 °C (5 mmHg)] was dried as previously described.[3] 18-Crown-6 (Fluka) was purified according to ref 1. Pretreated THF[12] was distilled over a sodium–potassium alloy in an atmosphere of dry argon. Toluene was dried over metallic sodium and then distilled under an argon atmosphere. Isotactic PMMA (Polymer Laboratories) was used as received. Predominantly atactic and syndiotactic PMMA were prepared in our laboratories.[13]

Measurements. The NMR spectra were recorded using a Varian VXR-300 multinuclear spectrometer. The ^{1}H and ^{13}C NMR spectra were run in $CDCl_3$ by using TMS as an internal standard. Number-average molecular weights were determined in $CHCl_3$ using a Knauer vapor pressure osmometer. GPC experiments were conducted in a THF solution at 35 °C at a flow rate of 1 mL/min using a Spectra-Physics 8800 solvent delivery system with 10^4-, 10^3-, and 500-Å Styragel columns in series and a Shodex SE 61 refractive index detector. Polystyrene standards having a low polydispersity (PL Laboratories) were used to generate a calibration curve. DSC measurements were performed using a DSC DuPont 1090B (thermal analyzer) apparatus at a heating rate of 20 °C/min.

Preparation of PMMA Macroinitiators via Partial Saponification of PMMA. A total of 10 g of PMMA was dissolved in 100 mL of dry toluene containing the required amount of 18-crown-6 complex of potassium hydroxide. After completion of the reaction, conducted at room temperature, the polymer was precipitated in hexane, filtered off, washed with dry methanol, dried under vacuum, and stored under argon.

Synthesis of Poly[(methyl methacrylate)-*co*-(benzyl methacrylate)]. The average number of the carboxylate anion initiating sites, formed by partial saponification of PMMA, and the efficiency of the saponification reaction were determined for a sample of macroinitiators through reaction with benzyl bromide. Partially saponified PMMA (1 g) was dissolved in 10 mL of dry THF, and benzyl bromide was added into the reaction mixture in small molar excess. The reaction was conducted for 10 h at room temperature. The copolymer formed was precipitated in methanol, filtered off, dried under high vacuum, and characterized by GPC, VPO, and ^{1}H NMR techniques (see Figure 3).

The efficiency of the saponification reaction, determined on that basis was 87–95%.

General Procedure of Grafting of β-Butyrolactone onto PMMA. The grafting of β-butyrolactone on a PMMA backbone containing various amounts of carboxylate active species was conducted at a temperature of 20 °C in a THF solution. The PMMA macroinitiator, obtained and pretreated as described above, was introduced under an argon atmosphere into the reaction vessel and dissolved in dry THF. Then the desired amount of β-BL was added. The progress of the grafting was followed using ^{1}H NMR. After its completion the reaction was quenched by addition of methyl iodide. The graft polymer obtained was precipitated in methanol, filtered off, dried in vacuum, and characterized using GPC, VPO, and NMR techniques. The dried graft polymer was extracted with methanol (a good solvent for atactic β-butyrolactone homopolymer) upon stirring 2 h. However, after filtration the composition of graft polymer was found to be unchanged, as revealed by ^{1}H NMR analysis.

The procedure was repeated to produce graft polymers of different composition and molecular weight (see Table 1).

Results and Discussion

Graft copolymers containing a polyacrylate backbone and polyester pendant groups were previously synthesized *via* direct anionic grafting of pivalolactone on the polyacrylate backbone.[9] In this procedure, the carboxylate groups were generated in the polyacrylate polymer due to the saponification of pendant ester groups. After addition of the pivalolactone monomer, the graft copolymers with polyester pendant groups were prepared. However, formation of pivalolactone homopolymer (3.8–12%) was also observed.[9]

It was demonstrated in our previous works that in the anionic polymerization of β-butyrolactone propagation proceeds *via* carboxylate active centers and in the presence

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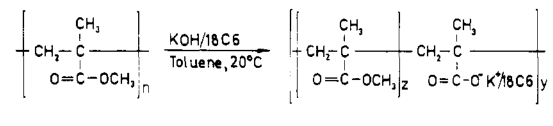
Table 1. Results of the Anionic Grafting of β-Butyrolactone on a Poly(methyl methacrylate) Backbone

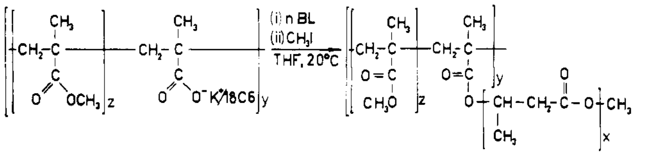
sample no.	PMMA tacticity[a]	composn of P (β-BL)[b] (%)	yield (%)	$M_n \times 10^{-3}$ calc[c]	$M_n \times 10^{-3}$ est[d]	y[e]	M_nz[f]	M_nx[g]
1	isotactic	44	79	10.5	10[h]	7	800	600
2	syndiotactic	71	92	57.2	58	13	1300	3000
3	syndiotactic	74	95	62.3	60	35	440	1240
4	atactic	45	97	132.6	126	65	1100	840

[a] Sample 1 was obtained to β-BL grafting on isotactic PMMA while samples 2 and 3 were prepared using predominantly syndiotactic PMMA and sample 4 was obtained from predominantly atactic PMMA, respectively. [b] mol % estimated by ^{1}H NMR. [c] Number-average molecular weight of graft copolymer calculated according to the formula (4). [d] Number-average molecular weight of graft copolymer estimated from GPC. [e] Average number of graft sites calculated from eq 2a. [f] The number-average molecular weight of the PMMA backbone between grafting sites calculated according to eq 1. [g] The number-average molecular weight of the poly(β-butyrolactone) side chains from eq 3. [h] Determined by VPO technique in $CHCl_3$.

Scheme 1



Scheme 2



of a crown ether or cryptand "living" polymers are produced.[3,4,6]

The present paper illustrates the utility of the PMMA macroinitiator bearing carboxylate ions complexed by 18-crown-6 potassium counterions for anionic grafting of β-butyrolactone onto a poly(methyl methacrylate) backbone in a controlled fashion.

Synthesis of Poly(methyl methacrylate) macroinitiator. Poly(methyl methacrylate) (PMMA) macroinitiator was prepared *via* controlled saponification of pendant ester groups with potassium hydroxide/18-crown-6 (1:1)[14] (Scheme 1).

The macroinitiator obtained was separated from the reaction mixture, as described in the Experimental Section, before being used for β-butyrolactone polymerization.

Anionic Grafting of β-Butyrolactone on Poly(methyl methacrylate). It has been demonstrated that partly saponified PMMA having carboxylate ions complexed by 18-crown-6 potassium counterion acts as a macroinitiator of β-butyrolactone polymerization. As a result a graft polymer of PMMA with grafted poly(butyrolactone) side chains is produced. After termination of the graft polymerization with methyl iodide, the methyl ester groups were formed as the end groups of poly(β-butyrolactone) chains (Scheme 2).

The resulting graft copolymers, possessing a comblike structure with a random distribution of atactic poly(β-butyrolactone) segments on a polymethacrylate backbone, were characterized by NMR (Figure 1) and GPC (Figure 2).

In the ^{1}H NMR spectra of graft polymers obtained both signals corresponding to PMMA repeating units and those of poly(β-butyrolactone) segments at δ = 1.3 (CH_3), 2.3–2.8 (CH_2), and 5.0–5.4 (CH) were observed (Figure 2). The total composition of graft polymers was estimated by ^{1}H NMR, based on integrals of characteristic signals of poly(β-butyrolactone) segments (d or e, Figure 1) and those of overlapping signals of methoxy ester groups (c and c′, Figure 1).[15]

The absence of β-butyrolactone homopolymer was excluded by GPC and selective extraction experiments. The GPC analysis showed a decrease of the unimodal signal of graft copolymer retention volume (Figure 2b) as compared with that of starting PMMA (Figure 2a). The selective extraction of graft polymer in methanol, conducted as described in the Experimental Section, revealed also that no β-butyrolactone homopolymer was formed. Moreover, no transfer graft reaction was observed as confirmed by a control experiment.[16]

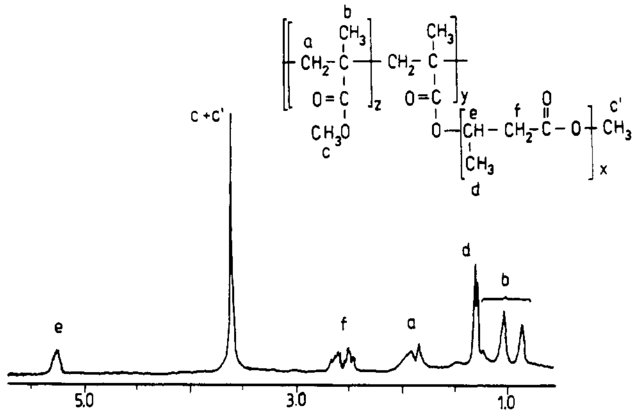


Figure 1. ^{1}H NMR of poly[(methyl methacrylate)-*g*-(β-hydroxybutyrate)].

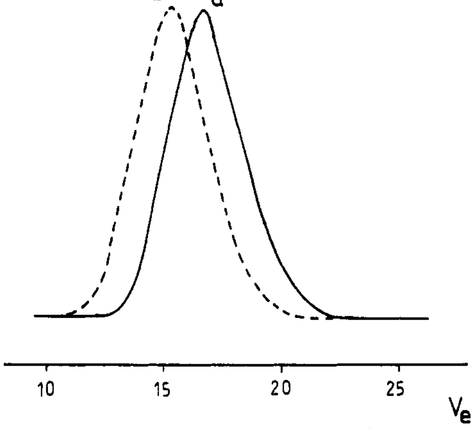


Figure 2. GPC traces of (a) poly(methyl methacrylate) [M_n(GPC) = 78 000] and (b) poly[(methyl methacrylate)-*g*-(β-hydroxybutyrate)] [M_n(GPC) = 126 000].

The length of blocks in a graft copolymer defined by x, y, and z (Figure 1), where x is the average number of the β-hydroxybutyrate repeating units in the grafted chains, y refers to the average number of grafting sites, and z is the average number of MMA units between grafting sites, were estimated as follows.

In order to estimate y and z in the obtained graft polymers (see Figure 1), a simple model polymer has been synthesized (Figure 3) *via* benzylation of the PMMA macroinitiator.[17] The model copolymer of methyl methacrylate and benzyl methacrylate (BMA) so obtained was

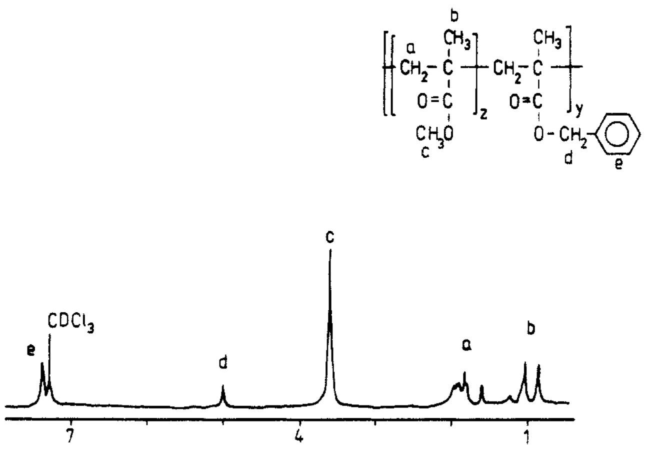


Figure 3. ^{1}H NMR spectrum of poly[(methyl methacrylate)-*c*-(benzyl methacrylate)].

characterized by GPC and ^{1}H NMR (Figure 3). Besides the signals corresponding to the PMMA repeating units, those of benzyl methacrylate units at $\delta = 5.1$ (CH_2) and 7.3 (C_6H_5) were also observed (Figure 3). Since H^1 integration of protons in methoxy groups (c, Figure 3) to protons in benzylmethylene groups (d, Figure 3) in P(MMA-*co*-BMA) gives the average number of unsaponified MMA units per BMA unit (z, from Figure 3), the number-average molecular weight of the PMMA backbone consisting of z units was calculated according to the formula:

$$M_{nZ} = zM_{MA} \quad (1)$$

where M_{MA} is the molecular weight of methyl meth acrylate.

The average number of carboxylate initiating sites, equal to y (Figure 3), was calculated as the ratio of the number-average molecular weight of the copolymer (determined by GPC) to the sum of the number-average molecular weight of the PMMA backbone between grafting sites (M_{nZ}) and the molecular weight of benzyl methacrylate:

$$y = M_{nC}/(M_{nZ} + M_{BA}) \quad (2a)$$

where M_{nC} is the number-average molecular weight of poly[(methyl methacrylate)-*c*-(benzyl methacrylate)] determined by GPC analysis and M_{BA} is the molecular weight of benzyl methacrylate. Alternatively, it can also be calculated based on the molecular weight of the starting PMMA according to the formula:

$$y = M_{nPMMA}/[M_{MA}(z + 1)] \quad (2b)$$

where M_{nPMMA} is the number-average molecular weight of the starting poly(methyl methacrylate).

The values of M_{nZ} and y for PMMA macroinitiators saponified to varying degrees are presented in Table 1.

The average numer of poly(β-butyrolactone) units in the grafted chains (x, Figure 1) was estimated from the ^{1}H NMR spectrum of the graft polymer obtained using the corresponding values of z calculated as described above. The number-average molecular weight of poly(β-butyrolactone) chains (M_{nX}) was therefore calculated according to the formula:

$$M_{nX} = xM_{BL} \quad (3)$$

where x is the average number of P(β-BL) repeating units determined by ^{1}H NMR (Figure 3) and M_{BL} is the molecular weight of β-BL.

Because the validity of the universal calibration principle for characterizing branched polymers by GPC has been questioned, especially with comblike polymers,[18] the number-average molecular weight of the graft polymers obtained was calculated according to the formula:

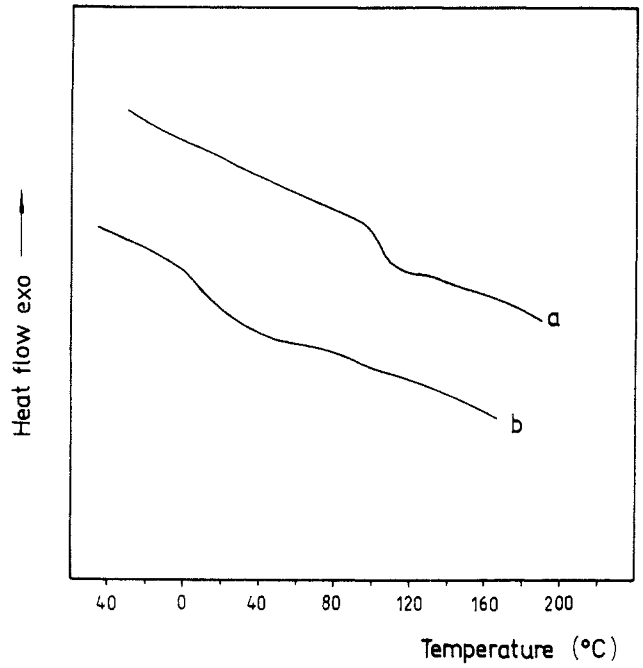


Figure 4. DSC curves of (a) poly(methyl methacrylate) and (b) the corresponding poly[(methyl methacrylate)-*g*-(β-hydroxybutyrate)] (sample 4, Table 1).

$$M_n = y(M_{nZ} + M_{nX} + M_{MA}) \quad (4)$$

It turned out, however, that calculated values for polymers obtained were in good agreement with that obtained by GPC using polystyrene standards calibration and VPO measurements (Table 1). This is most probably due to the fact that the number-average molecular weight of β-BL branches is relatively low as compared with that of PMMA.

The results obtained for β-butyrolactone anionic grafting on poly(methyl methacrylate) with different molecular weights and structures are summarized in Table 1.

The analysis of the ^{13}C NMR spectra of the graft polymers obtained confirmed that poly(β-butyrolactone) segments are atactic.[3]

The preliminary DSC measurements for the graft polymer containing 45% of P(β-BL) revealed the single glass transition temperature located at 25 °C (Figure 4b). The T_g value for the corresponding PMMA homopolymer is equal to 105 °C (Figure 4a), and T_g values determined for atactic poly(β-butyrolactone) were found to be molecular weight dependent up to 15 000 M_n, however, were always observed below 4 °C.[4,19] Further studies of thermal and mechanical properties of new graft polymers obtained are under way.

Conclusions

It has been found that anionic grafting of β-butyrolactone on PMMA can be performed, without side reactions, over a fairly wide composition range (10–80% poly(β-BL)).

The synthesis of such graft polymers is remarkably simple as compared with those described previously.[9] The graft efficiency is high (up to 98%), and the density of grafting can be easily determined.

The described synthetic approach enables the synthesis of "tailormade" graft copolymers via anionic polymerization of β-lactone monomers on carboxylate propagation centers with alkali-metal counterions complexed by macrocyclic ligands.

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References and Notes

(1) Jedliński, Z.; Kurcok, P.; Kowalczuk, M. *Macromolecules* **1985**, *18*, 2679.

(2) Jedliński, Z. In *Handbook of Polymer Synthesis*; Kricheldorf, H. R., Ed.; Marcel Dekker Inc.: New York, 1992; Part A, p 645.

(3) Jedliński, Z.; Kowalczuk, M.; Kurcok, P.; Kasperczyk, J. *Makromol. Chem.* **1986**, *187*, 1651.

(4) Jedliński, Z.; Kowalczuk, M.; Kurcok, P.; Brzoskowska, L.; Franek, J. *Makromol. Chem.* **1987**, *188*, 1575.

(5) Głowinkowski, S.; Kapturczak, J.; Pajak, Z.; Kurcok, P.; Kowalczuk, M.; Jedliński, Z. *Polymer* **1989**, *30*, 519.

(6) Jedliński, Z.; Kowalczuk, M.; Kurcok, P. *J. Macromol. Sci., Pure Appl. Chem.* **1992**, *A29* (12), 1223.

(7) Ballard, D. G. H.; Bowles, R. J.; Haddleton, D. M.; Richards, S. N.; Sellens, R.; Twose, D. L. *Macromolecules* **1992**, *25*, 5907.

(8) Lucas, E. F.; Porter, R. S. *J. Appl. Polym. Sci.* **1993**, *49*, 1211.

(9) Sundet, S. A.; Thamm, R. C.; Meyer, J. M.; Buck, W. H.; Caywood, S. W.; Subramanian, P. M.; Anderson, B. C. *Macromolecules* **1976**, *9*, 371.

(10) Zhou, P.; Frisch, H. L. *J. Polym. Sci., Polym. Chem.* **1993**, *30*, 2577.

(11) Lenz, R. W. In *Advances in Polymer Science*; Springer-Verlag: Berlin, 1993; Vol. 107, p 1.

(12) Weissberger, W. *Organic Solvents*; Wiley-Interscience: New York, 1970; p 704.

(13) Czech, A.; Gaska, B.; Janeczek, H.; Jedliński, Z. Polish Pat. Appl. P-300058, 1993.

(14) Dietrich, B.; Lehn, J. M. *Tetrahedron Lett.* **1973**, *15*, 1225.

(15) Kricheldorf, H. R.; Scharnagl, N. *J. Macromol. Sci. Chem.* **1989**, *A26*, 951.

(16) No transfer graft reaction, which might have caused the increase of a number of branched points, decreasing the actual molecular weight of graft branches, was demonstrated by the following control experiment. The mixture of unsaponified PMMA (M_n = 35 000) with PMMA macroinitiator containing 10% of saponified methyl ester groups (derived from PMMA possessing M_n = 169 000) was subjected to grafting with β-BL in THF. After termination of the grafting reaction with methyl iodide the GPC analysis revealed that the retention volume of the chromatographic peak corresponding to the unsaponified PMMA remained unchanged.

(17) Liotta, C. L.; Harris, H. P.; McDermott, M.; Gonzales, T.; Smith, P. *Tetrahedron Lett.* **1974**, *28*, 2417.

(18) Dreyfuss, P.; Quirk, R. P. In *Encyclopedia of Polymer Science and Engineering*; Mark, H., Bikales, N., Overberger, C., Menges, G., Eds.; John Wiley & Sons: New York, 1987; Vol. 7, p 568.

(19) Adamus, G.; Kowalczuk, M.; Jedliński, Z. *J. Polym. Mater.* **1993**, *10*, 83.