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Synthesis and characterization of amphipathic poly(methyl methacrylate)-b-poly(ethylene oxide) diblock copolymers

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Summary

This paper describes the synthesis and characterization of amphipathic diblock copolymers of poly(methyl methacrylate) (PMMA) and poly(ethylene oxide) (PEO). The synthesis involved the coupling of acyl chloride-terminated PMMA block with methoxy poly(ethylene oxide) (MPEO). Carboxylic acid chloride-terminated PMMA was generated by treating with thionyl chloride the parent carboxylic PMMA, which was prepared by free radical polymerization of methyl methacrylate (MMA) using benzoyl peroxide (BPO) as the initiator and β-mercaptopropionic acid (MPA) as the chain transfer agent. The proposed mechanism of MMA polymerization is in good agreement with the experimental results which indicate that as a side reaction nonfunctional (aromatic) counterpart is produced in a small quantity. The coupling of the acyl chloride-terminated PMMA with MPEO was quantitative.

Introduction

Amphipathic block copolymers are of great interest for academic research as well as for industrial applications. When in possession of appropriate structural features for the system, these copolymers can be effective colloid stabilizers. Their use in heterogeneous polymerizations, and as compatibilizers in blends has shown great promise (1).

Four general approaches have been reported in the literature for the preparation of amphipathic block copolymers. These are coupling of individually synthesized components, living ionic (anionic or cationic) polymerizations, macroradical initiations, and post-polymerization modification methods. Kennedy and Hongu (2,3) have used the coupling technique to synthesize polyisobutylene/PEO diblock and triblock copolymers. Galin and Mathis (4), also using the coupling method, have reported the preparation of poly(dimethylsiloxane)/PEO triblock copolymers. Living anionic polymerization was used by Riess et al. (5,6) and Khan et al. (7) to synthesize polystyrene-b-PEO copolymers, and by Tomoi et al. (8) to prepare poly(alkyl methacrylate)-b-PEO block copolymers. Macroradical initiation has been used by several investigators for the preparation of PMMA-b-PEO (9-11) and for polystyrene-b-PEO block

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coploymers (12,13). An example of post-polymerization modification is the preparation of amphipathic poly(vinyl alcohol-acetate) which is obtained by partial alcoholysis of poly(vinyl acetate) with methanol.

In our study, the synthesis of PMMA-b-PEO diblock copolymers was carried out via a novel coupling route, which permitted the preparation of well-defined block structure.

Experimental

Materials

MMA was purified by vacuum distillation at 22°C. BPO, MPA, and thionyl chloride were reagent grade and used as received. Triethylamine (TEA) was doubly distilled with phthalic anhydride followed by potassium hydroxide. MPEOs were vacuum dried at 80°C for 24 hrs prior to use. Toluene and benzene were distilled over a sodium dispersion in paraffin immediately before use.

Measurements

FTIR spectra were recorded on a Beckmann FT 2100 spectrometer. Proton NMR spectra were measured on a Varian Gemini FT 200 spectrometer. GPC chromatograms were determined with a Waters 150C ALC/GPC using Styragel columns and THF as the mobile solvent.

Preparation of Carboxylic PMMA

The MMA in toluene solution (1 mol in 80 ml) containing various amounts of MPA (0.06-0.40 mol) was polymerized using BPO (0.02 mol) as the initiator. The polymerizations were carried out at 85°C for 24 hrs under nitrogen blanket. A solvent-precipitant (acetone-heptane) fractionation technique was applied to fractionate as well as purify the product. The molecular weights of PMMA fractions were determined both by titration with 0.01N potassium hydroxide in ethanol and by proton NMR using deuterated chloroform as the solvent. An FTIR spectrum was recorded for one of the carboxylic PMMA fractions.

Synthesis of PMMA-b-PEO Diblock Copolymers

The carboxylic acid terminated PMMA (0.06 mol, $M_n = 500$ g/mol) was dissolved in 100 ml of freshly distilled benzene. Thionyl chloride (0.90 mol) was then added, and the contents of the flask was allowed to reflux at 85°C for 24 hrs to generate the acid chloride-terminated PMMA. In another flask, MPEO (0.03 mol, $M_n = 750$ g/mol) was dissolved in freshly distilled toluene, and TEA (0.06 mol) was added slowly with syringe. The contents of the two flasks were combined and allowed to undergo coupling at 65°C for 8 hrs. Upon completion, the contents were filtered to remove the insoluble TEA-HCl salt. The crude product was precipitated in heptane. The PMMA-b-PEO diblock was purified by solvent-coagulant (acetone-heptane) fractionation, and then vacuum dried. Finally, the resulting diblock was analyzed by FTIR, proton NMR, and GPC analysis.

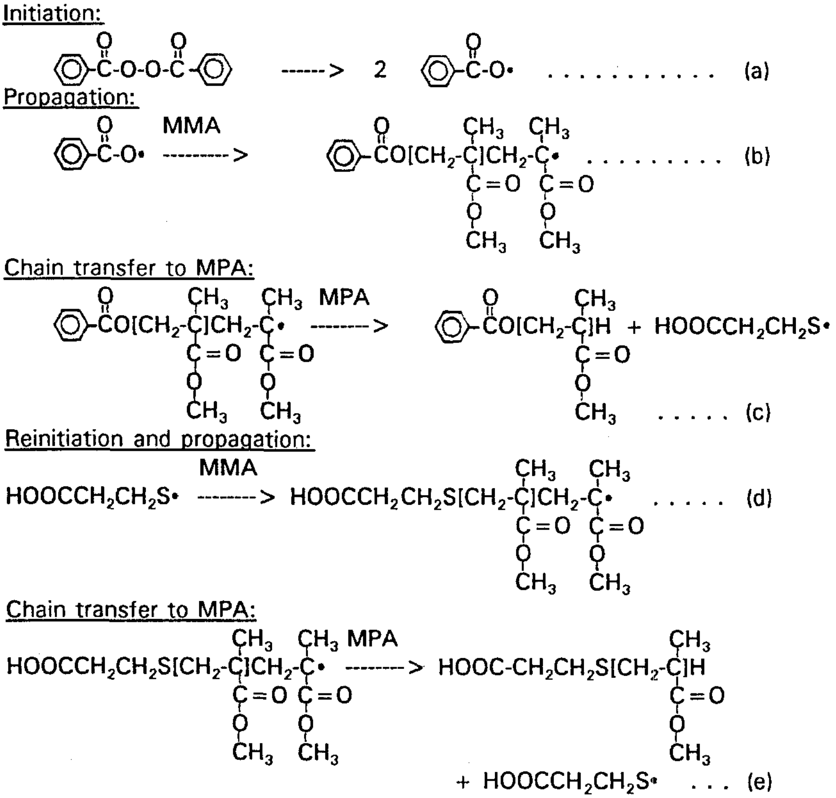
Results and Discussion

In this study the coupling technique was used for the preparation of PMMA-b-PEO diblock copolymers by reacting acyl chloride-terminated PMMA with methoxy PEO.

1. Preparation and Characterization of Carboxylic PMMA

The carboxylic PMMA was prepared by free radical polymerization of MMA initiated by BPO. The molecular weight was controlled by chain transfer with MPA. The proposed reaction mechanism is presented in Scheme 1: the primary radicals from BPO decomposition initiate and propagate with MMA until chain transfer to MPA occurs. The chain transfer reaction creates mercapto radicals which reinitiate and propagate with MMA until chain transfer to another MPA takes place. Propagations (b) and (d) are competing steps that generate nonfuctional (aromatic) and functional (carboxylic) PMMA through chain transfer steps (c) and (e), respectively. As a result, a mixture of functional and nonfunctional PMMA molecules is created.

Scheme 1. Polymerization Mechanism for Preparing Carboxylic PMMA



A typical FTIR spectrum for a carboxylic PMMA fraction is displayed in Figure 1. This spectrum shows a broad, weak O-H stretching band due to terminal carboxylic acid over the 3300-2500 cm^{-1} region, onto which are superimposed three aliphatic C-H stretching peaks at 3000, 2950, and 2850 cm^{-1}, respectively. The two C=O carbonyl peaks, one from the ester group in the methyl methacrylate units and the other from the terminal carboxyl group, overlap at 1730-1710 cm^{-1}. In addition, an aromatic C-H out-of-plane bending peak appears at 730 cm^{-1}, indicating the formation of a mixture of carboxylic (functional) and aromatic (nonfunctional) PMMAs.

The proton NMR spectrum for a carboxylic PMMA fraction is shown in Figure 2 along with the chemical shift assignments (14,15). The molecular weight of the carboxylic

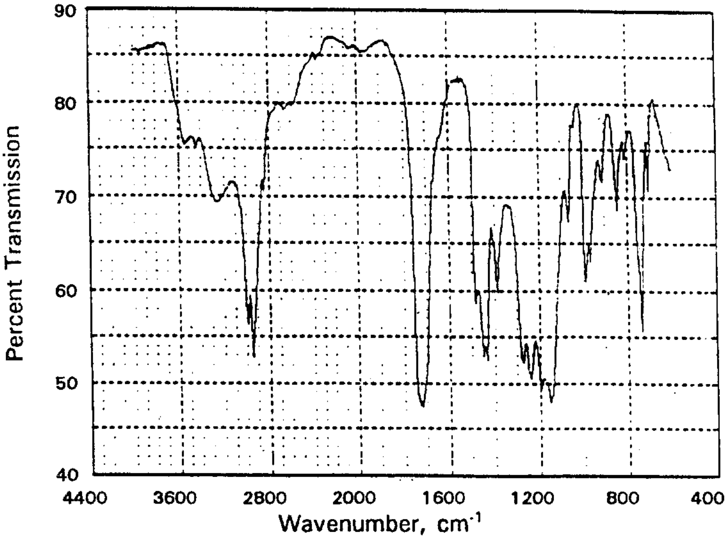


Figure 1. FTIR Spectrum of Carboxylic PMMA Fraction

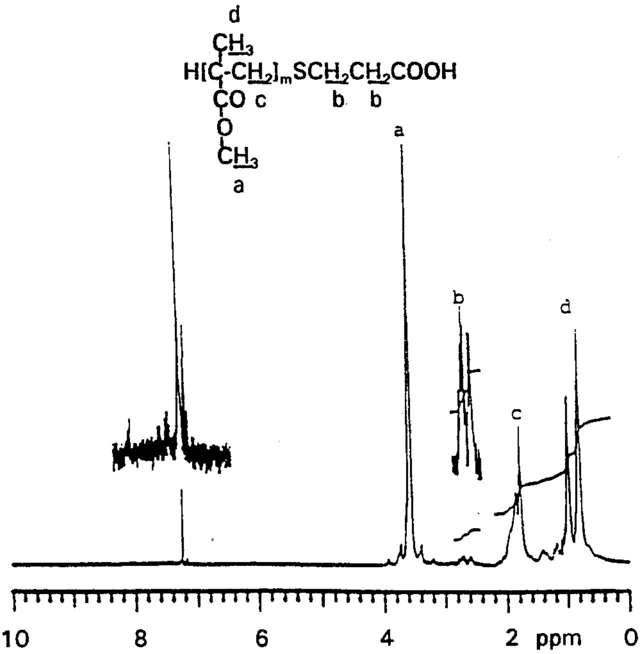


Figure 2. Proton NMR Spectrum of Carboxylic PMMA Fraction

PMMA is determined from the integration ratio between the peaks at 2.7 and 2.6 ppm due to methylene protons in MPA ($-SC\underline{H}_2C\underline{H}_2COO-$) and the peaks at 1.8, 0.9, and 0.8 ppm due to backbone protons in PMMA. Aromatic protons were observed clearly in the expanded spectrum in the downfield region. This also revealed that the PMMA fractions actually contained a small amount of nonfunctional counterparts. The results of the preparation of carboxylic PMMA are summarized in Table 1.

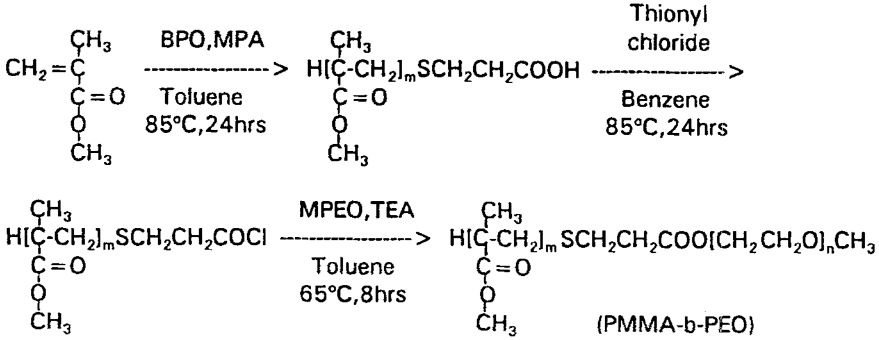
Table 1. Molecular Weight of Carboxylic PMMA Fractions

Molar Ratio MMA/BPO/MPA	Code for PMMA Fraction	M_n(g/mol) Titration	M_n(g/mol) H^1 NMR
50/1/3	PMMA3-1F	4300	3600
	PMMA3-2F	3800	
	PMMA3-3F	3000	
50/1/5	PMMA5-1F	2800	
	PMMA5-2F	2500	2300
	PMMA5-3F	2000	
50/1/7	PMMA7-1F	2000	
	PMMA7-2F	1700	1900
	PMMA7-3F	1400	
50/1/12	PMMA12-1F	1100	1200
	PMMA12-2F	900	
	PMMA12-3F	800	
50/1/20	PMMA20-1F	600	
	PMMA20-2F	500	500
	PMMA20-3F	450	

2. Synthesis and Characterization of PMMA-b-PEO Diblock Copolymers

A coupling approach was used to prepare PMMA-b-PEO diblock copolymers by reacting acyl chloride-terminated PMMA with MPEO. The overall synthesis route is illustrated in Scheme 2. The FTIR spectra in Figure 3 represents the resulting PMMA-b-PEO diblock copolymer in (a) and the starting MPEO homopolymer in (b). These two spectra show strong C-H stretching at 2900 cm^{-1} and symmetric C-O-C

Scheme 2. Synthesis Route for PMMA-b-PEO Diblock Coplymers



$$CH_2{=}C(CH_3)COOCH_3 \xrightarrow[\text{Toluene, }85^\circ C,\text{ 24hrs}]{\text{BPO,MPA}} H[C(CH_3)(COOCH_3)\text{-}CH_2]_mSCH_2CH_2COOH \xrightarrow[\text{Benzene, }85^\circ C,\text{ 24hrs}]{\text{Thionyl chloride}}$$

$$H[C(CH_3)(COOCH_3)\text{-}CH_2]_mSCH_2CH_2COCl \xrightarrow[\text{Toluene, }65^\circ C,\text{ 8hrs}]{\text{MPEO,TEA}} H[C(CH_3)(COOCH_3)\text{-}CH_2]_mSCH_2CH_2COO[CH_2CH_2O]_nCH_3$$

(PMMA-b-PEO)

stretching within the PEO block at 1100 cm^{-1}. However, the diblock copolymer shows a strong C=O carbonyl absorption at 1730 cm^{-1} which is absent in the MPEO homopolymer.

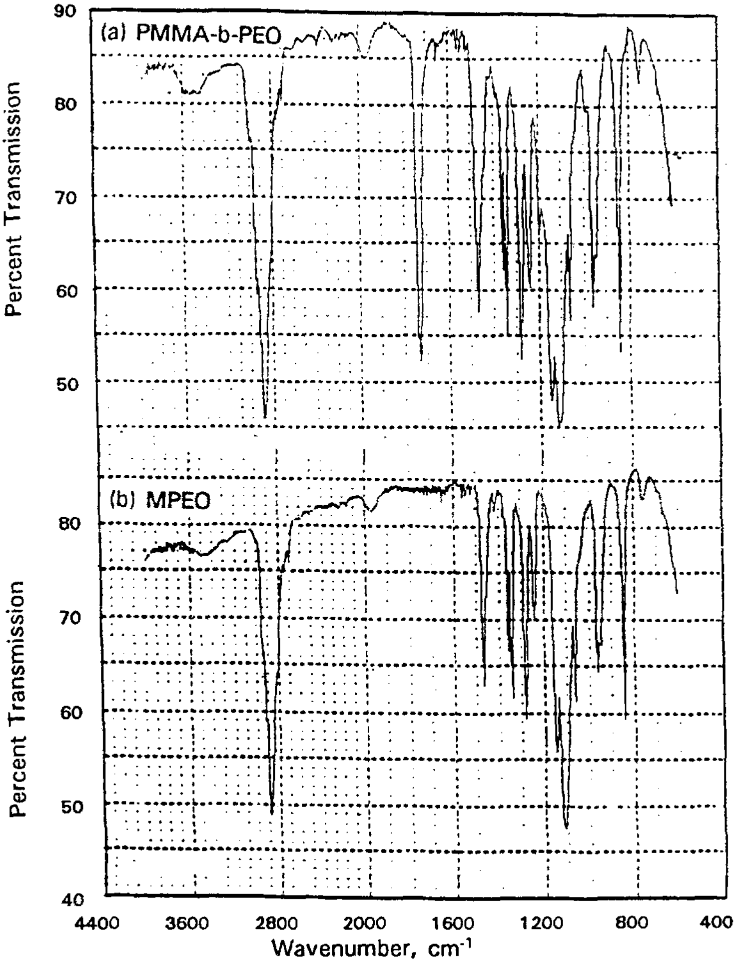
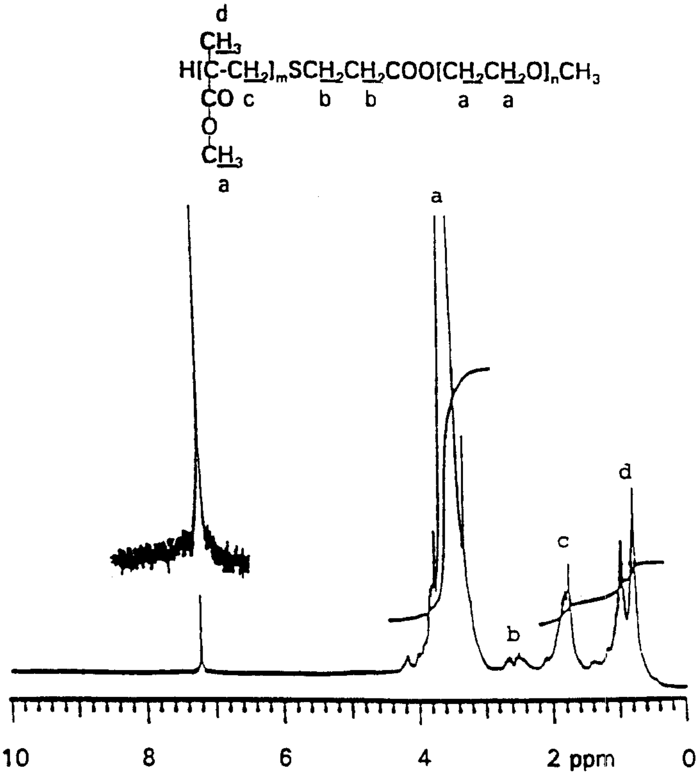


Figure 3. FTIR Spectra of PMMA-b-PEO Diblock Copolymer (a) and MPEO Homopolymer (b)

Figure 4 shows a typical proton NMR spectrum for PMMA-b-PEO diblock copolymer prepared by coupling between acid chloride and hydroxyl groups. Compared to the spectrum for PMMA block in Figure 2, the proton NMR spectrum for the diblock copolymer shows a much stronger resonance peak at 3.7 ppm due to the methylene protons in PEO (-C$\underline{H}_2$C$\underline{H}_2$O-). Obviously, the resonance of the methylene protons of the PEO block falls in the same region as that of the ester methyl protons of PMMA block. Since the two groups cannot be separately recorded, the composition of the block copolymers had to be determined from the integration ratio between the peak at 3.7 ppm due to the overlapping of PEO methylene protons and PMMA methyl ester protons, and the peaks at 1.8, 0.9, and 0.8 ppm due to PMMA backbone protons. In this determination, of course, the number-average molecular weight of MPEO block has to be known.



$H[C(C\underline{H}_3)(COOC\underline{H}_3)-C\underline{H}_2]_mSC\underline{H}_2C\underline{H}_2COO[C\underline{H}_2C\underline{H}_2O]_nCH_3$

Figure 4. Proton NMR Spectrum of PMMA-b-PEO Diblock Copolymer

A complete listing of ten PMMA-b-PEO diblock copolymers prepared by this method can be found in Table 2. The table also lists the weight percent PEO in the molecule determined by ^{1}H NMR spectroscopy, and the MWD as obtained by GPC measurements. The formation of the amphipathic PMMA-b-PEO diblock coploymers has been verified since they show surface activity in aqueous solutions and they are effective polymeric surfactants in emulsion polymerizations (16).

Table 2. Molecular Structure of PMMA-b-PEO Diblock Copolymers

M_n(PMMA) (g/mol)	M_n(PEO) (g/mol)	Total MW (g/mol)	Wt(%)PEO (^{1}H NMR)	MWD(M_w/M_n) (GPC)
PMMA-b-PEO(750) Diblock Series				
400	750	1150	65	1.33
900	750	1650	46	1.29
PMMA-b-PEO(2000) Diblock Series				
400	2000	2400	83	1.22
800	2000	2800	71	1.19
1300	2000	3300	61	1.29
PMMA-b-PEO(5000) Diblock Series				
400	5000	5400	93	1.13
800	5000	5800	86	1.15
1200	5000	6200	81	1.19
1900	5000	6900	72	1.20
2500	5000	7500	67	1.18

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