Polymer Bulletin 24, 363–370 (1990)

Polymer Bulletin

# Graft copolymers of poly(methyl methacrylate) backbone and poly(propylene oxide-b-ethylene oxide) branches

## Synthesis and characterization

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## Summary

Two mono-functional macromonomers of poly(propylene oxide-b-ethylene oxide) were synthesized by reaction with methacryloyl chloride. The macromonomers have the same molecular weight and ratio of ethylene oxide and propylene oxide sequences. The reactive methacrylate group can be linked to the ethylene oxide (BuPPOPEO) or to the propylene oxide (BuPEOPPO). These macromonomers showed self-gelling in one week even at low temperature and under a dry atmosphere. Graft copolymers were obtained by reaction of these macromonomers with methyl methacrylate upon free-radical initiation and they were characterized by GPC, VPO, IR and $^1$H NMR spectra.

## Introduction

The diblock copolymers of ethylene oxide and propylene oxide exhibit surfactant properties in solution (1). Graft copolymers comprising chemically dissimilar sequences yield intramolecular phase separation and lead to a number of specific applications (2). Some investigations have already emphasized the properties of graft copolymers in solution, due to their high molecular weight (3).

Several works about graft copolymers using macromonomers have been published (4-6) and some macromonomers can homopolymerize (self gelling polymers)(7-8). In this case, the polymers spontaneously form irreversible gels in water as soon as the degree of the polymerization exceeds a certain limit and

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*To whom correspondence should be addressed this critical degree of polymerization decreases when the molecular weight of the monomers increase.

The purpose of this work is to synthesize the macromonomers in a different way and to get graft copolymers of poly(methyl methacrylate) backbone with poly(propylene oxide-b--ethylene oxide) branches by radical copolymerization.

## Experimental

### Materials

Commercial mono-functional poly(propylene oxide-b--ethylene oxide) samples (Grupo Ultra) of $\overline{M}_n$=920 and $\overline{M}_n$=900 were azeotropically dried in toluene. Methacryloyl chloride was prepared by reaction between methacrylic acid and benzoyl chloride. Methyl methacrylate was purified by vacuum distillation. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Toluene and benzene were dried by distillation over Na.

### Preparation of macromonomers

Poly(propylene oxide-b-ethylene oxide) methyl methacrylate macromonomers were synthesized in accord with a paper about self-gelling polymers (7). To a well stirred solution of BuPEOPPO or BuPPOPEO and pyridine in toluene, cooled in a water-ice bath, the methacryloyl chloride was added very slowly. After all the chloride had been added, the solution was stirred for 1 h at 0°C, and for 16 h more at room temperature. After decanting, the produced pyridine.HCl salt was separated by filtration at reduced pressure under nitrogen flow. Toluene and pyridine were evaporated under vacuum. The macromonomers were used quickly or stored at 0°C up to 5 days under dry atmosphere.

### Copolymerization of macromonomer with methyl mathacrylate

Methyl methacrylate, macromonomer, benzene and AIBN were introduced into a polymerization apparatus under nitrogen flow (3 minutes). The solvent volume was about twice the monomer volume and AIBN was used at concentration of 0.3 mol/mol of monomers. Polymerization took place under heating at 80°C for 48 h. The resultant viscous solution was poured into a large excess of n-hexane and the white precipitate was filtered and vacuum dried. The copolymer was purified by reprecipitation from toluene into n-hexane, filtered and vacuum dried.

### Copolymers conversion curves

Radical copolymerization of BuPPOPEO with methyl methacrylate was carried out with AIBN (0.3 mol/mol of monomers) and benzene (80% wt/v). The homogeneous mixture of macromonomer, comonomer, initiator and solvent was equally divided into nine parts and copolymerized in glass tubes under a nitrogen atmosphere, at 75°C, for several copolymerization times, to get time-conversion data (9).

## Measurement

Number average molecular weights of polymers ($\overline{M_n}$) were measured on a Wescan 232 A vapor pressure osmometer (VPO) in toluene at 60°C. Gel permeation chromatography (GPC) was performed on Micronal chromatography equipped with columns 50-100-500 Å using THF as eluent and the chromatograms were calibrated against standard poly(propylene oxide) samples to analyse the commercial samples. To the copolymers it was used gel permeation chromatography Waters 200 with columns 500-3000-10000-300000 Å, using THF as eluent and the chromatograms were calibrated against standard polystyrene samples. IR spectra were recorded with a Nicolet-740 FTIR spectrometer and $^1H$ NMR spectra were recorded on Bruker AC 200 MHz (BuPPOPEO and BuPEOPPO) and on Varian VXR-300 apparatus (copolymers).

## Results and discussion

Our research group have worked with macromonomers from poly(ethylene oxide) and poly(propylene oxide) with several molecular weights and we have obtained and stored them as it is presented in a preceding paper (4). Only poly(ethylene oxide) methyl methacrylate, $\overline{M_n}$=600, forms spontaneously irreversible gels even at low temperature, probably because it contains more reactive groups per molecule. The same macromonomer, $\overline{M_n}$=1000, did not show gelling under the same conditions (10). In the case of BuPEOPPO and BuPPOPEO, $\overline{M_n}$=900, self-gelling was observed in one week at 5°C. Probably, there are chemical-physical interactions between the like sequences bringing the reactive groups near to each other.

The diblock copolymers (BuPPOPEO and BuPEOPPO) were analysed to establish the number of ethylene oxide and propylene oxide repeat units through $^1H$ NMR spectroscopy (Fig. 1 and Table 1).

The formation of macromonomers was observable by the infrared spectrum, as illustrated in Fig. 2. The IR spectrum of BuPPOPEO methyl methacrylate exhibits a characteristic ester carbonyl absorption at 1720 $cm^{-1}$ due to end methacrylate group which is absent in the IR spectrum of BuPEOPPO.

The macromonomers were copolymerizated with methyl methacrylate. The results are presented in Table 2.

The graft copolymers were purified by sucessive reprecipitations in toluene/hexane, as presented in Fig. 3. No peaks are observable in the lower molecular weight region due to the presence of macromonomer. It is important to observe

Table 1: Characterization of diblock copolymers of BuPPOPEO and BuPEOPPO

| Copolymer | Molecular weight | | | Repeat units [c] | |
|---|---|---|---|---|---|
| | $\overline{M}_n$ [a] | $\overline{M}_w/\overline{M}_n$ [a] | $\overline{M}_n$ [b] | EO | PO |
| BuPPOPEO | 747 | 1.23 | 900 ± 15 | 6 | 10 |
| BuPEOPPO | 835 | 1.28 | 920 ± 15 | 6 | 10 |

[a] Determined by GPC. [b] Determined by VPO. [c] Determined by $^1H$ NMR spectroscopy.

Table 2: Radical copolymerization of poly(propylene oxide-b-ethylene oxide) macromonomer ($M_1$) with methyl methacrylate ($M_2$)

| Run | Feed | | | | Graft copolymers | | |
|---|---|---|---|---|---|---|---|
| | Macromonomer | $M_1$ g | $M_2$ g | $[M_2]/[M_1]$ mole/ratio | Yield wt% | $M_1$ [a] wt% | $\overline{M}_n$ [b] |
| 1 | BuPEOPPO | 3.34 | 25 | 80 | 81 | 12 | 43714 |
| 2 | BuPEOPPO | 4.45 | 25 | 60 | 79 | 15 | 65722 |
| 3 | BuPEOPPO | 6.68 | 25 | 40 | 76 | 18 | 80848 |
| 4 | BuPPOPEO | 6.68 | 50 | 80 | 91 | 11 | 78439 |
| 5 | BuPPOPEO | 8.90 | 50 | 60 | 89 | 14 | 84524 |
| 6 | BuPPOPEO | 13.36 | 50 | 40 | - | 20 | 67340 |

[a] Determined by $^1H$ NMR spectroscopy. [b] Determined by VPO in toluene.

that this purification was possible because even if any macromonomer had not polymerized its concentration in solution would be low. Solubility tests showed that BuPPOPEO was insoluble in hexane at higher concentration.

The formation of graft copolymers was also observable by the infrared spectrum, as illustrated in Fig. 4. The IR spectrum of macromonomer (Fig. 4b) exhibits a characteristic ester carbonyl absorption at 1720 $cm^{-1}$ and absorptions at 2962-2872 $cm^{-1}$ (stretching bands of $CH_3$ group) and 1150 $cm^{-1}$ (asymmetrical C-O-C stretching). The spectrum of poly(methyl methacrylate)

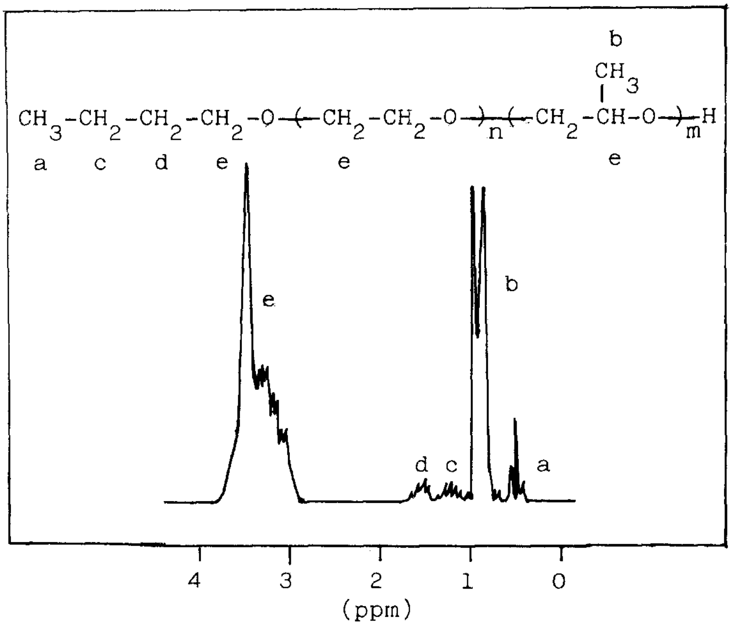

Fig. 1. $^1$H NMR spectrum of BuPEOPPO in $CDCl_3$

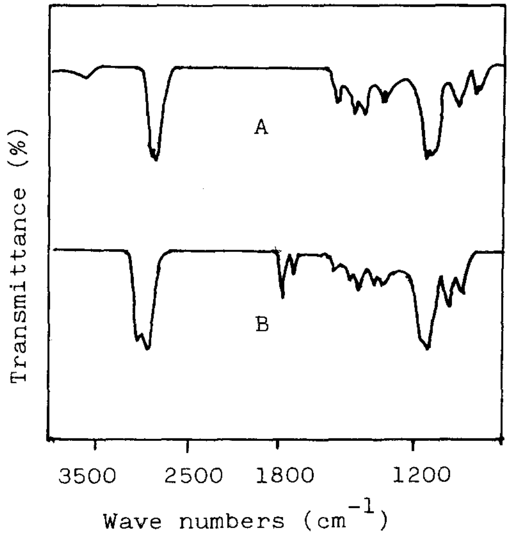

Fig. 2. Infrared spectra of A, BuPEOPPO; B, BuPEOPPO methyl methacrylate.

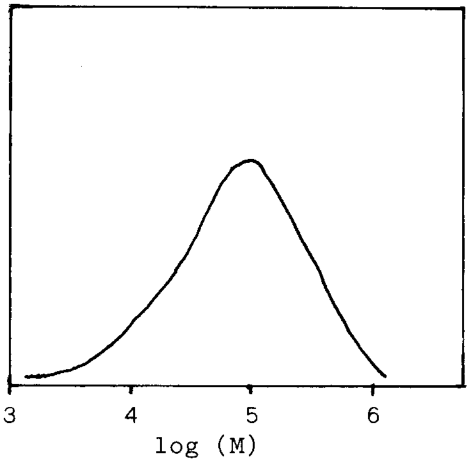

Fig. 3. GPC curve of graft copolymer. Solvent: THF; temp.: 25°C. Run 4 in Table 2.

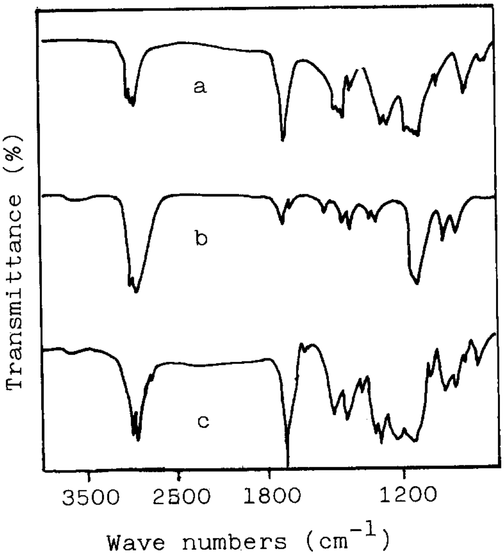

Fig. 4. Infrared spectra of a, PMMA; b, macromonomer BuPEOPPO; c, run 1 in Table 2.

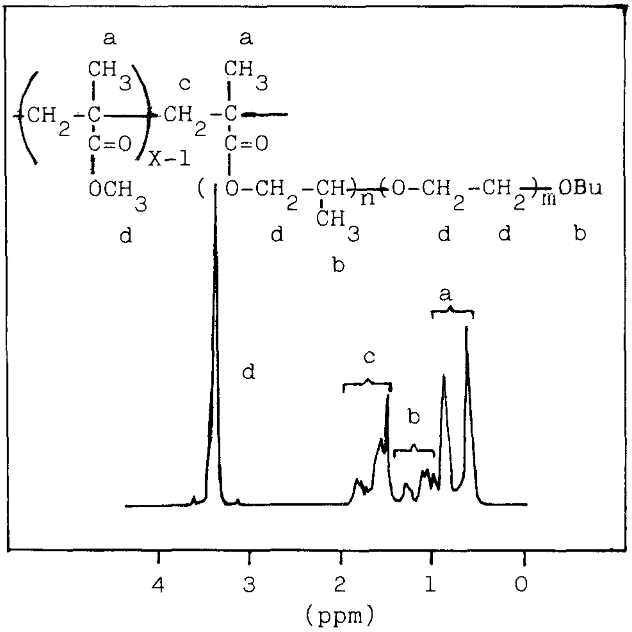

Fig. 5. $^1H$ NMR 300 spectrum of graft copolymer in $CDCl_3$ (Run 1 in Table 2)

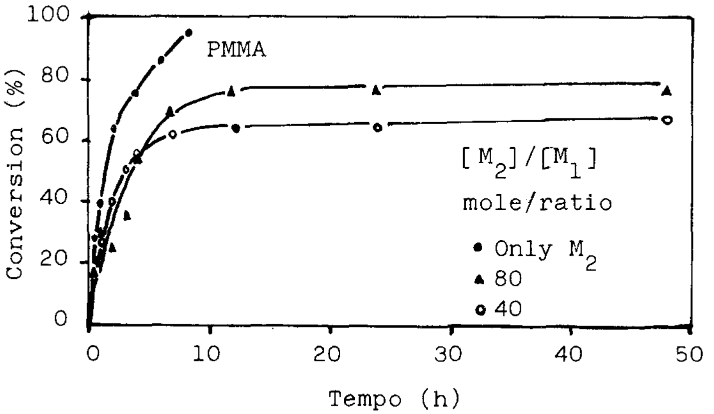

Fig. 6. Time-conversion curves of BuPPOPEO methyl methacrylate ($M_1$) and MMA ($M_2$) in the copolymerization. Solvent: benzene; temp.: 75°C; initiator: AIBN.

(Fig. 4a) shows bands at 2930 $cm^{-1}$ (symmetrical stretching $-CH_2-$) and at 1160 $cm^{-1}$ (asymmetrical stretching band $-C-C{\genfrac{}{}{0pt}{}{=O}{-O}}$). The spectrum of the graft copolymer (Fig. 4c) shows broader peaks at 2950 $cm^{-1}$ and 1150 $cm^{-1}$ due to absorptions of both poly(methyl methacrylate) and poly(propylene oxide-b-ethylene oxide).

The quantitative analysis of graft copolymer composition can be calculed from $^1H$ NMR spectrum peak intensities (Fig. 5). The percentages of BuPEOPPO and BuPPOPEO in the copolymer is 92000/Ms and 90000/Ms, respectively, as described in a preceding paper (4) where Ms is the molecular weight of the recurring unit.

Results of copolymerization of BuPPOPEO methyl methacrylate ($M_1$) with MMA ($M_2$) carried out in two different ratios ($[M_2]/[M_1]=80$ and 40 mole/ratio) are shown in time conversion curves of the copolymers in Fig. 6. It can be seen from these and from other data which have already been published that the copolymer conversion percentage is directly related to the macromonomer quantity and to the macromonomer molecular weight. Probably, the interpenetration of a macromonomer chain in the coil of the propagating comonomer radical, would cause these differences in the conversion (9).

## Acknowledgment

This work was supported by Financiadora de Estudos e Projetos (FINEP), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPQ), Conselho de Ensino para Graduados e Pesquisa (CEPG-UFRJ) and Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ).

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Accepted June 19, 1990 K