Polymer Bulletin 22, 401–406 (1989)

Polymer Bulletin

Poly(methyl methacrylate-g-propylene oxide)

1. Synthesis and characterization

Clara Marize F. Oliveira* and Ailton S. Gomes

Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro, C.P. 68525, Rio de Janeiro, Brazil

Summary

Graft copolymers with uniform poly(propylene oxide) grafts were synthesized by the radical copolymerization of poly(propylene oxide) methacrylate macromonomers and methyl methacrylate. The macromonomers were prepared by reaction of bifunctional poly(propylene oxide) and methacryloyl chloride. The graft copolymers were readily soluble in chloroform, tetrahydrofuran and toluene at room temperature. Copolymers with 23% of poly(propylene oxide) grafts were soluble in hot methanol and above this composition were soluble in methanol at room temperature. The graft copolymers were characterized by GPC, viscometry, IR and ^{1}H NMR spectra.

Introduction

The synthesis of graft copolymers by the macromonomer technique has been of interest because it produces graft chains which only vary in their frequency of attachment to the backbone (1-4). Several publications concern the incorporation of graft chains into poly(methyl methacrylate) by the macromonomer technique (5-7). Previously, we reported the synthesis of poly(propylene oxide) methacrylate macromonomer, by reaction of bifunctional poly(propylene oxide) and methacryloyl chloride. The product formed was characterized by high performance liquid chromatography and was found to contain 56% of poly(propylene oxide), 41% of poly(propylene oxide) mono methacrylate and 3% of dimethacrylate macromonomers (8).

This paper describes the radical copolymerization of methyl methacrylate with poly(propylene oxide) macromonomers to produce soluble graft copolymers.

Experimental

Materials

Methacryloyl chloride was prepared by reaction between

*To whom correspondence should be addressed

methacrylic acid and benzoyl chloride. Methyl methacrylate was purified by removal of inhibitors and distillation as usual. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Toluene, benzene and tetrahydrofuran (THF) were dried by distillation over Na.

Synthesis and characterization of macromonomers

Poly(propylene oxide) methyl methacrylate macromonomers were synthesized as described in a preceding paper (8). Bifunctional poly(propylene oxide) of $\overline{M}_n$=2470 was azeotropically dried in toluene and reacted with methacryloyl chloride in toluene/pyridine. The produced pyridine.HCl salt was separated by filtration at reduced pressure under nitrogen flow. Toluene and pyridine were removed in a rotary evaporator. Products of reaction were isolated by preparative high performance liquid chromatography (Hewlett Packard model 1084 B with a refractive index detector and a silica gel column - Zorbax-Sil, 250x4.3 mm) in ethyl acetate.

Synthesis and purification of graft copolymers

To a solution of benzene and 1/5 of AIBN at 80ºC, under nitrogen atmosphere, was added the mixture of methyl methacrylate macromonomers and 3/5 of AIBN, at a rate of approximately 1 ml/minute. After 6 h of reaction the remaining 1/5 of catalyst was added and the reaction was continued for 8 more hrs. The resultant viscous solution was poured into a large excess of n-heptane and the white precipitate was filtered and vacuum dried. The copolymer was purified by reprecipitation from chloroform into n-heptane, filtered and vacuum dried. The copolymer was free of macromonomer as confirmed by means of GPC using refractive index methods (Toyo Soda high-speed liquid chromatography HLC-803 A, with THF as eluent and using a polystyrene calibration curve).

The graft copolymers were fractioned by precipitation of the copolymer solution in toluene with n-heptane, at 25ºC. The initial solution concentration was 1% (w/v) and the fractions were separated by decantation after successives additions of the precipitant.

Characterization of graft copolymers

The copolymers were characterized by IR, ^{1}H NMR, GPC and viscometry. IR spectra of copolymer films were recorded with a Perkin Elmer 467 infrared spectrophotometer and ^{1}H NMR spectra were recorded on Varian XL-100 apparatus. The viscosities were measured in THF at 23ºC using an Ostwald 50 viscometer.

Results and discussion

The purpose of this investigation was to establish whether the radical copolymerization of a mixture of macromonomers of poly(propylene oxide) mono-and dimethacrylate with methyl methacrylate monomer could be carried out to yield soluble graft copolymers. These macromonomers were not separated from poly-(propylene oxide) to prepare the graft copolymers. The reaction conditions and results are presented in Table 1.

Table 1: Radical copolymerization of mixed poly(propylene oxide) macromonomers (M_1) with methyl methacrylate (M_2)

Run	Feed			Graft copolymers		
	PPO[a]- M_1 mixture g	M_2 g	$[M_2]/[M_1]$ mole/ratio	Yield wt%	M_1[b] wt%	$[\eta]$[c]
1	21.4	30	80	84	20	0.25
2	28.4	30	60	80	23	0.27
3	42.8	30	40	74	32	0.36
4	57.0	20	20	55	51	0.63

[a] PPO - Poly(propylene oxide). Experimental conditions: temp.: 80ºC; solvent: benzene; initiator: AIBN (0.3 mol% to monomers); duration: 16 h. [b] Determined by ^{1}H NMR spectroscopy. [c] Measured in THF at 23ºC.

The graft copolymers were freed of macromonomers and poly-(propylene oxide) by successive reprecipitations in chloroform/n-heptane, as presented in Fig. 1. The small peak is assigned to the unreacted macromonomers and it is observable in the lower molecular weight region. Since the homopolymer of macromonomers was not obtained under the same conditions of copolymerization reactions, we concluded that this homopolymer was absent or it was soluble in n-heptane.

In the fractional precipitations of the product all the fractions showed the characteristic absorptions of both PMMA and poly(propylene oxide) as seen from ^{1}H NMR spectra; thus we concluded that PMMA homopolymer was not formed. Fig. 2 shows the results of fractional precipitations of all graft copolymers (runs 1-4 in Table 1) and PMMA (for comparison). The cumulative percentage of the precipitated fractions is plotted as a function of γ, the volume fraction of the precipitant added. When the grafted branches in the copolymer are higher the precipitant volumes are also higher.

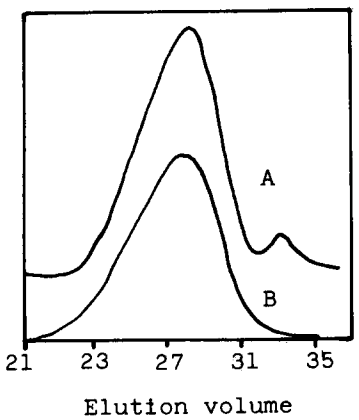

Fig. 1. GPC curves of graft copolymer (solvent, THF; temperature, 30ºC). A, Polymer recovered after radical copolymerization; B, polymer recovered after three successive reprecipitations.

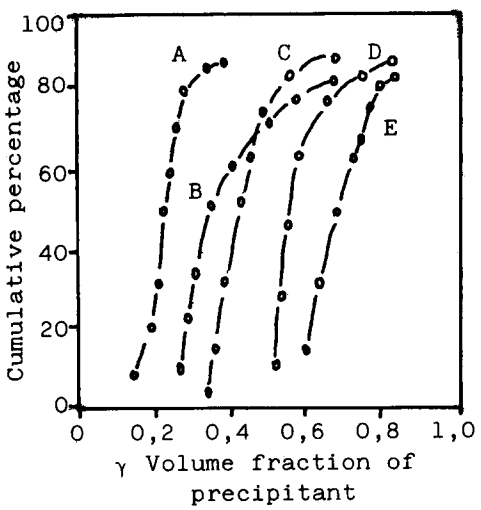

Fig. 2. Curves of fractional precipitations. A, PMMA; B,run 1; C,run 2; D,run 3; E,run 4 in Table 1. Solvent, toluene; precipitant, n-heptane; temp. 25ºC

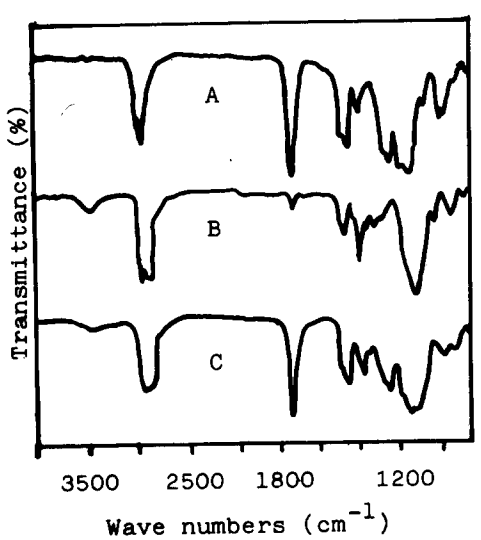

Fig. 3. Infrared spectra of A, PMMA; B, product of synthesis of macromonomers; C, run 4 in Table 1.

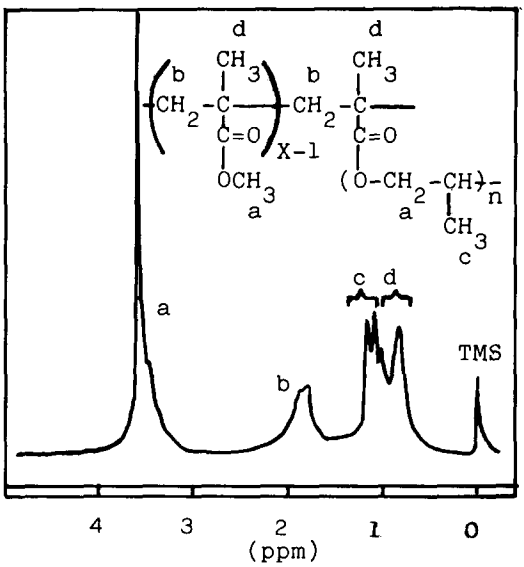

Fig. 4. ^{1}H NMR spectrum of graft copolymer in $CDCl_3$ obtained by radical copolymerization of poly(propylene oxide) methyl methacrylate macromonomer and MMA (run 2 in Table 1).

The formation of graft copolymers were also observable by the infrared spectrum, as illustrated in Fig. 3. The IR spectrum of a mixture of macromonomers and poly(propylene oxide)(Fig. 3b) exhibit a characteristic hydroxyl absorption at 3480 cm^{-1}, an 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 PMMA (Fig. 3a) shows bands at 2930 cm^{-1} (symmetrical stretching band $-CH_2-$) and at 1160 cm^{-1} (asymmetrical stretching band -C-C=O-). The spectrum of the graft copolymer (Fig. 3c) shows broader peaks at 2950 cm^{-1} and 1150 cm^{-1} due to absorptions of both PMMA and poly(propylene oxide).

All peaks assigned to PMMA and poly(propylene oxide) segments were observed in the ^{1}H NMR spectrum of the graft co - polymers as shown in Fig. 4. The composition of the graft co - polymer can be calculed from peak intensities (9). Let the average number of ^{1}H NMR units per grafted chain of poly- (propylene oxide) be X, the number of protons in poly(propylene oxide) N, the sum of the resonance area at a, c, d in Fig. 4 A and resonance area b B, it follows that

$$A \alpha 6X + N - 3$$
$$B \alpha 2X$$

For poly(propylene oxide) having $\overline{M}_n$=2470, n=42, N=253 and

$$A/B = 3 + 125/X$$

The percentage of poly(propylene oxide) in copolymer is

$$100\ M/Ms$$

where Ms is the molecular weight of the recurring unit according to the equation

$$Ms = 100\ X - 31 + M$$

where 31 is the molecular weight of the $-OCH_3$ group and M is the average molecular weight of the poly(propylene oxide) chains. The percentage of the poly(propylene oxide) in the copolymer is then 247000/Ms.

Intrinsic viscosities of graft copolymers increased with the increase in the percentage of grafting. Studies on the solution properties of these graft copolymers are in progress at Instituto de Macromoléculas.

This work was supported by Financiadora de Estudos e Projetos (FINEP), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPQ) and Conselho de Ensino para Graduados e Pesquisa (CEPG-UFRJ).

References

1. Milkovich R (1980) Polym Prep 21: 40
2. Vargas J-S, Franta E, Rempp P (1981) Makromol Chem 182: 2603
3. Cameron G-G, Chisholm S-M (1985) Polymer 26: 437
4. Gramain P, Frère Y (1987) Makromol Chem 188: 593
5. Kennedy J-P, Misao H (1983) J Polym Sci Chem 21: 1033
6. Schulz G-O, Milkovich R (1984) J Polym Sci Chem 22: 1633
7. Smith S-D, McGrath J-E (1986) Polym Prep 27: 31
8. Gomes A-S, Oliveira C-M-F, Lourenço V-L In press J Polym Sci Chem
9. Twaik M-A, Tahan M, Zilkha A (1969) J Polym Sci A-1,7: 2469

Accepted September 13, 1989 K