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Polyacrylonitrile-graft-poly(ethylene oxide)

1. Synthesis and characterization of copolymers obtained in *N,N*-dimethyl formamide solution

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Summary

Graft copolymers of polyacrylonitrile (PAN) and poly(ethylene oxide) (PEO) were synthesized by radical copolymerization of acrylonitrile and methacrylate-headed poly(ethylene oxide) macromonomer. The macromonomer was prepared by reaction of methacryloyl chloride with PEO. The effects of solution concentration, initiator concentration and acrylonitrile/macromonomer molar ratio on the conversion, molecular weight and PEO branch content in the graft copolymer were studied. The graft copolymers were characterized by GPC, FTIR, ^{13}C-NMR and Kjeldhal method.

Introduction

Because of the high melting point, high melt viscosity and poor thermal stability of PAN, acrylonitrile (AN) must be copolymerized with other monomers like acrylates in order to achieve desirable polymer properties. Such copolymers have been used in a number of fields, such as synthetic fibers, thermoplastic elastomers, or barrier polymers (1). One application of PAN is in membrane process, for example, in the separation of water/ethanol by pervaporation (2). In this case, the hydrophilic character of PAN can be improved by copolymerization with other hydrophilic monomers (3-4).

Copolymers of PAN and PEO have been synthesized. The supermolecular structure of acrylonitrile-(ethylene oxide) block copolymers, synthesized with a redox system have been studied by Kwiatkowski et *al.* (5). Graft copolymers of PAN and PEO have been obtained by the macromonomer method in homogeneous dimethyl sulfoxide (DMSO) solution at 60°C. In this case the graft copolymers were obtained over a broad range of compositions and molecular weights [$M_w \sim (0.5 - 9.0) \times 10^5$] (6).

Graft copolymer with well-controlled structure has been obtained by copolymerization of macromonomer with a comonomer. The macromonomer component forms the branches with controlled length (7).

In this work graft copolymers of PAN and PEO were synthesized by the macromonomer method in homogeneous N,N-dimethyl formamide (DMF) solution at 65°C. The copolymers were characterized by usual techniques.

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Experimental

Materials

PEO (Aldrich) of M_n = 1,400 (Knauer vapor pressure osmometer in chloroform at 25°C) was azeotropically dried in toluene. Methacryloyl chloride was prepared from methacrylic acid and benzoyl chloride (8). Acrylonitrile (Vetec) was distilled as usual, using phosphoric acid to remove the inhibitors. DMF (Rio Lab), analytical grade, was used without distillation. N-Methyl-2-pyrrolidone (NMP) (Aldrich, 99%) was used without distillation. 2,2'-Azobisisobutironitrile (AIBN) was recrystallized from methanol. Toluene was dried by distillation over Na.

Synthesis and characterization of macromonomers

Methacrylate-headed PEO macromonomer was prepared by reaction of PEO with methacryloyl chloride in toluene solution containing pyridine. After filtration of pyridine salt, toluene and pyridine were removed in a rotary evaporator. The reaction products were isolated by high performance liquid chromatography (Waters chromatograph with Waters 410 IR detector and three Ultrastyragel columns) in chloroform at 25°C. The product was found to contain 51% of PEO and 49% of a mixture of macromonomers of PEO mono- and dimethacrylate.

Synthesis and purification of graft copolymers

A solution of macromonomer, AN, and AIBN in DMF was placed in a reactor equipped with reflux condenser under N_2 flow. The initiator concentration was varied between 0.3-1.5 mol% of monomers and the AN/macromonomer molar ratios were 20, 50, 60 and 80. In all cases, the resulting solution was poured in a large excess of distilled water, the yellow precipitate was filtered, washed with ethanol, and dried in an oven at 65°C to constant weight. The reactions were made in duplicate. The copolymers were purified by reprecipitation from DMF in distilled water (1/10 v/v). Gel permeation chromatography (GPC) was used to confirm that the copolymers were free of macromonomer (Waters Styragel columns - 10^3Å and 10^4Å) in NMP/10^{-2}M LiBr solutions as eluent at 50°C. Apparent molecular weights and polydispersity indices were calculated using polystyrene calibration.

Characterization of graft copolymers

The copolymers were characterized by IR, ^{13}C-NMR, GPC and Kjeldhal method. Infrared spectra of copolymer films were recorded using a Perkin-Elmer 1720X FT-IR spectrometer and ^{13}C-NMR spectra were obtained with a Varian Gemini 300 apparatus. Quantitative composition determination of graft copolymers was measured by using the Kjeldhal method for nitrogen (9). The PEO branch content was determined after calculating the AN content, assuming that the sample was formed only by copolymerization.

Results and discussion

Graft copolymers with PAN backbone and PEO branches, obtained by radical copolymerization of AN and methacrylate-headed PEO macromonomer, were purified by successive reprecipitations in DMF/water to remove homopolymers of PEO and macromonomer, washed with ethanol, and dried until constant weight. Most of the graft copolymers were soluble in solvents for PAN like DMF, NMP, dimethyl acetamide and DMSO.

The formation of graft copolymer was confirmed by i.r. spectra (Fig. 1). The spectrum of PAN [Fig.1(a)] shows bands at 2940 cm^{-1} (symmetrical stretching band -CH$_2$-), at 2244 cm^{-1} (symmetrical stretching band -CN) and 1623 cm^{-1} (asymmetrical stretching band). The spectrum of PAN-graft-PEO [Fig. 1(b)] shows bands at 2940, 2244 and 1623 cm^{-1} due to absorptions of PAN, and bands at 1720 cm^{-1} (ester carbonyl absorption) and 1100 cm^{-1} (asymmetrical C-O-C stretching) due to methacrylate-headed PEO macromonomer. ^{13}C-NMR spectroscopy was also applied to characterize the graft copolymer. The peaks assigned to PAN and PEO are observed in Figure 2. The displacement relative to PAN segment are: 32.80 δ (CH$_2$) and 121.39 δ (C≡N), while 17.46 δ (CH$_3$), 32.80 δ (CH$_2$), 69.90 δ (C-O-C) and 175 δ (C=O) are relative to PEO branches.

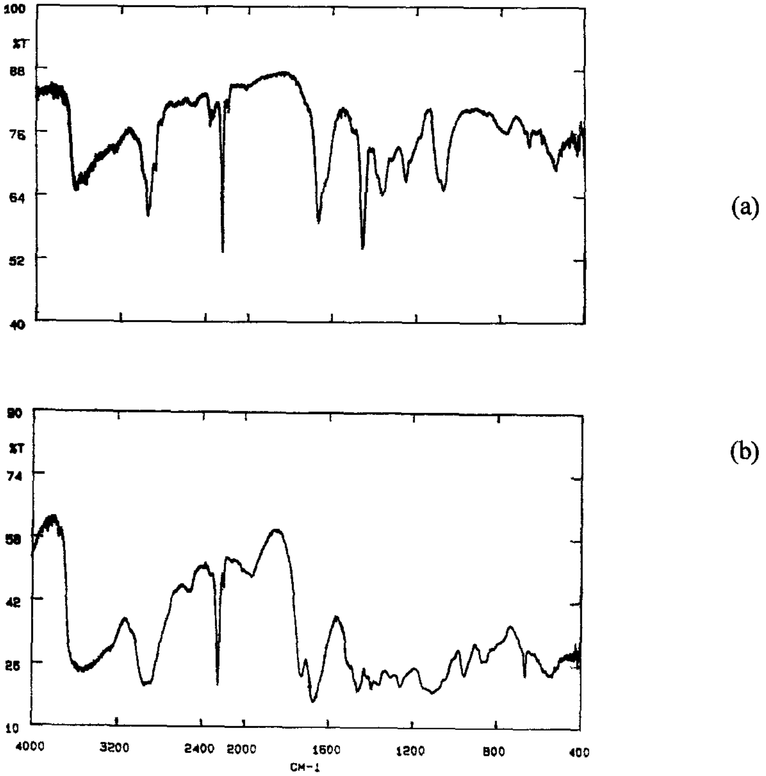

Fig. 1. Infrared spectra of polymers. (a) PAN obtained in DMF solution with AIBN initiator at 65°C, (b) PAN-graft-PEO (run 6) in Table 1.

In order to optimize the conditions for macromonomer grafting, the effects of solution concentration, initiator concentration, and AN/macromonomer molar ratio on conversion, molecular weight and PEO branch content in the graft copolymer are presented. Table 1 shows the effect of solution concentration and initiator concentration on the copolymerization of AN and methacrylate-headed PEO macromonomer. Table 2 shows the effect of AN/methacrylate-headed PEO macromonomer molar ratio on the copolymerization of AN and methacrylate-headed PEO macromonomer.

The results in Table 1 show that conversion and molecular weights increase with solution concentration. The molecular weight was more sensitive than conversion when comparing at the same initiator concentration. This fact is due to that more AN and macromonomer molecules can be added during the propagation step. Nevertheless, the PEO branch content in the copolymers was not affected by this variable.

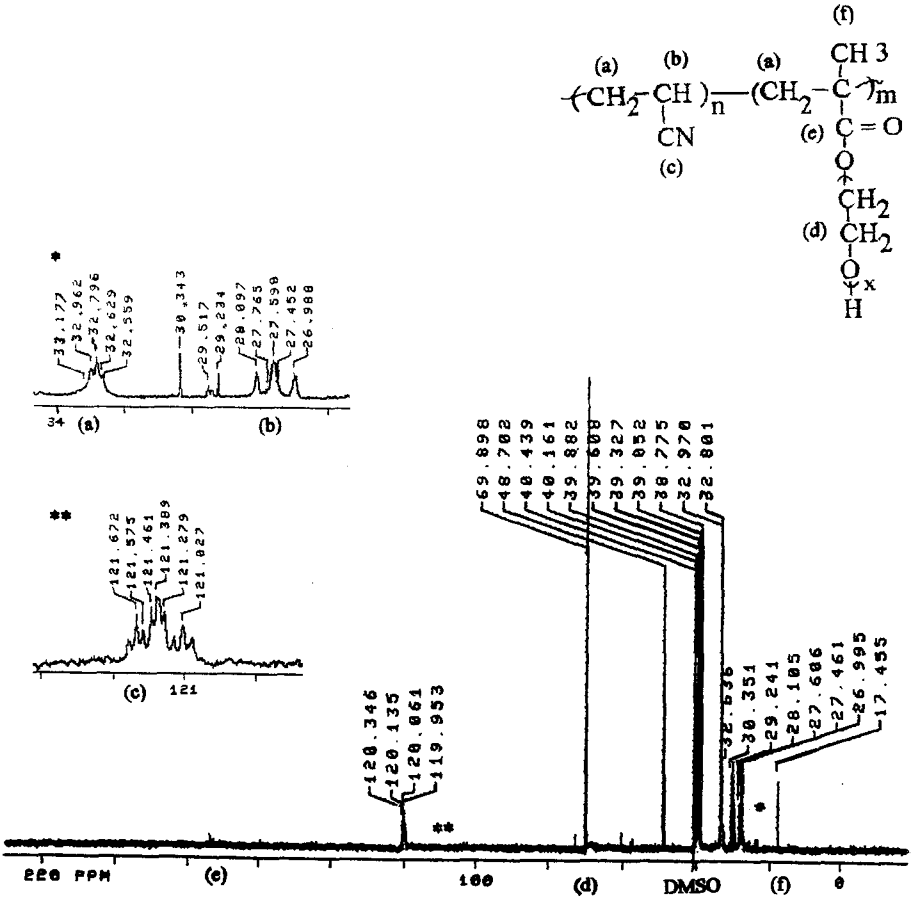

Fig.2. ^{13}CNMR spectrum of PAN-graft-PEO (run 9) in Table 2.

Table 1 - Effect of solution and initiator concentrations on the radical copolymerization of acrylonitrile (M_1) with methacrylate-headed poly(ethylene oxide) macromonomer (M_2)[a]

Run	M_1 (g)	M_2 (g)	AIBN (mol%)	Conversion (wt%)	M_w[b]	PEO[c] (wt%)
1	8.9	7.2	0.3	6	20,700	-
2	17.7	14.4	0.3	7	44,150	38
3	8.9	7.2	0.5	7	26,500	38
4	17.7	14.4	0.5	14	59,800	36
5	8.9	7.2	0.7	19	25,900	74
6	8.9	7.2	1.0	72	39,150	32
7	8.9	7.2	1.5	76	61,500	35

[a]Experimental conditions: temp.: 65°C; solvent: DMF (37.5 ml); time: 24 h. [b]Determined by GPC using polystyrene calibration and N-methyl-2-pyrrolidone/10^{-2}M LiBr solutions as eluent at 50°C. [c]Indirectly determined by Kjeldhal method for AN wt% content.

The effect of AIBN concentration on the conversion and molecular weight was less pronounced but increased with this variable. However at 1.0 mol% (run 6) of AIBN the conversion increased more pronounced, and the same effect was reflected in the molecular weight. The PEO branch content was not affected for these two variables (solution and initiator concentrations) ranging from 32 wt% (run 6) to 38 wt% (runs 2 and 3), although at 0.7 mol% AIBN the PEO branch content increased. In this case, run 5 was repeated in triplicate, and the PEO branch content of the products was around 74 wt%.

The behaviour of molecular weight shown in Table 2 in the range of 20-80 AN/macromonomer molar ratio was not affected, unless at molar ratio more rich in macromonomer (run 8). In this case, the molecular weight was the highest. This behaviour can be explained by the reactivity ratios of methyl methacrylate (1.322) and acrylonitrile (0.138) for low conversions (10). At the molar ratio more rich in macromonomer (run 8), AN incorporation predominates due to the methacrylate-headed PEO macromonomer may be upset methacrylate addition. For the other molar ratios predominate the methacrylate-headed PEO macromonomer incorporation, that is, the copolymers were more rich in PEO branch and they had lower molecular weight. At the molar ratios 50, 60 and 80 the molecular weight and PEO branch content were similar, and at molar ratio 60 the PEO branch content (86 wt%) and conversion (44 wt%) were maximum.

Table 2 - Effect of acrylonitrile (M_1)/methacrylate-headed poly(ethylene oxide) macromonomer (M_2) molar ratio on the radical copolymerization[a]

Run	M_1 (g)	M_2 (g)	M_1 / M_2 (mole/ratio)	Conversion (wt%)	M_w[b]	PEO[c] (wt%)
8	6.3	12.6	20	16	27,600	33
9	8.9	7.2	50	30	8,350	75
10	9.7	6.3	60	44	8,500	86
11	9.9	5.0	80	7	8,600	67

[a] Experimental conditions: temp.: 65°C; solvent: DMF (37.5 ml); time: 48 h. [b]Determined by GPC using polystyrene calibration and N-methyl-2-pyrrolidone/10^{-2}M LiBr solutions as eluent at 50°C. [c]Indirectly determined by Kjeldhal method for AN wt% content.

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References

1. Peng F-M (1985) Acrylonitrile polymers. In: Mark H, Bikales N-M, Overberger C-G (eds) Encyclopedia of Polymer Science and Engineering, Wiley-Interscience, New York (vol 1, pp 426-470)
2. Lee Y-M, Won K (1990) Polym J 22: 578
3. Yoshikawa M, Yukoshi T, Sanui K, Ogata N (1984) J Polym Sci Lett 22: 473
4. Jo W-H, Kim H-J, Kang Y-S (1994) J Appl Polym Sci 51: 529
5. Kwiatkowski R, Wlochowicz A, Wódka T (1990) Angew Makromol Chem 180: 145
6. Yan F, Déjardin P, Galin J-C (1990) Polym 31: 736
7. Schulz G-O, Milkovich R (1982) J Appl Polym Sci 27: 4773
8. Oliveira C-M-F, Lucas E-F (1990) Polym Bull 24: 363
9. Annual Book of ASTM Standards (1975) D 1013-70, American Society for Testing and Materials, Philadelphia (part 28, pp 219-220)
10. Simionescu C, Asandei N, Liga A (1967) Makromol Chem 110: 278