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Y. C. Yang[a]; J. C. Lim[a]; H. G. Woo[a]; S. K. Choi[a]
[a] Department of Chemistry, Korea Advanced Institute of Science and Technology, Chongyangni, Seoul, Korea

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Graft Copolymerization of Pyrrolidone onto Copolymers of N-Acryloyl Pyrrolidone and Vinyl Monomers

Y. C. YANG, J. C. LIM, H. G. WOO, and S. K. CHOI

Department of Chemistry
Korea Advanced Institute of Science and Technology
Chongyangni, Seoul, Korea

ABSTRACT

The copolymerizations of N-acryloyl pyrrolidone (NAP) with vinyl monomers methyl methacrylate (MMA), acrylonitrile (AN) and acrylamide (AA) were carried out in dimethylformamide at 65°C using 2,2'-azobisisobutyronitrile(AIBN) as an initiator. The resulting copolymers were used as a polymeric initiator of the anionic graft copolymerization of 2-pyrrolidone. The percent grafting of 2-pyrrolidone onto vinyl copolymer backbone chain involving N-acyllactam groups was found best with copoly(NAP-co-MMA) when the KOH concentration was 0.03 $\underline{M}$. The presence of crown ether increased the viscosity of graft copolymers and accelerated the initial rate of anionic graft copolymerization.

INTRODUCTION

The preparation and characterization of new graft copolymers has been a topic of interest for many investigators [1-4]. We have previously focused on the synthesis of new monomers with exocyclic groups which can serve as sites for various synthetic transformations.

It has been shown that backbone chains containing N-acylactam groups, which can act as promoters [5, 6], can be used for the synthesis of graft copolymers involving polyamide.

In a previous paper we reported a synthetic method of graft copolymers containing nylon-4 grafts onto the poly(N-acryloyl pyrrolidone-co-styrene) backbone. It was found that poly(NAP-co-St) can act as a polymeric initiator for the anionic graft copolymerization of 2-pyrrolidone [7].

In this work we report the effects of grafting time, KOH concentration, polymeric initiator, and crown ether [8, 9] on the graft copolymerization of 2-pyrrolidone onto the copolymers poly(NAP-co-MMA), poly(NAP-co-AN), and poly(NAP-co-AA).

EXPERIMENTAL

Materials

Potassium pyrrolidone salt and NAP were prepared by the method reported previously [7]. 18-Crown-6 ether was prepared and purified according to the literature [10]. Dibenzo 18-crown-6 (Aldrich Chemical Co.) was used without further purification. Monomers (Aldrich Chemical Co., Guaranteed reagents) and dimethylformamide were freshly redistilled under reduced pressure.

Procedure

Copolymerization of NAP with Vinyl Monomers

Freshly distilled NAP and vinyl monomers such as MMA, AN, and AA were added in various mole ratios in DMF to Pyrex ampules containing the required amount of AIBN initiator. The ampules were then sealed under vacuum and heated in a thermostat. When the polymerization was completed, the contents were precipitated into a large amount of methanol and the copolymers were filtered and dried at 60°C in vacuo overnight.

Grafting Procedure

The proper amounts of copolymers were dissolved in 2-pyrrolidone. The homogeneous solution was then transferred to a three-necked flask equipped with a magnetic stirrer and a nitrogen inlet. Purified nitrogen was passed for 1 h and then the required quantity of 2-potassium pyrrolidone salt was added. The reaction was carried out at 50°C under the nitrogen atmosphere. Methanol was added at the end of the required reaction time to terminate the polymerization. Copolymers were extracted in boiling water for 3 h in order to remove the homopyrrolidone oligomer.

The grafting percentage was calculated as follows:

$$\%\ \text{grafting} = \frac{\text{dry wt of grafted sample - dry wt of original sample}}{\text{dry wt of original sample}} \times 100$$

The viscosity of the graft copolymer was measured in sulfuric acid at 25°C using an Ubbelohde viscometer. The graft copolymer was identified by ^{1}H-NMR and IR. The composition of each monomer in the copolymer was calculated by elemental analysis.

RESULTS AND DISCUSSION

Copolymerization of NAP with Vinyl Monomers

The copolymerization of NAP with vinyl monomers such as MMA, AN, and AA was carried out in DMF at 65°C. Copolymer composition data for NAP-MMA, NAP-AN, NAP-AA copolymers are listed in Tables 1, 2, and 3. The method of Fineman and Ross was used to calculate the reactivity ratio values. The polarity parameter e and the resonance parameter Q values of each monomer pair were obtained by introducing the reactivity ratio values to Alfrey-Price equations. The results of these calculations are shown in Table 4. The values of r_1r_2 products for NAP and vinyl monomers were found to be greater than that of NAP and styrene reported in a previous paper [7]. The results are in the following order:

Poly(NAP-co-MMA) > Poly(NAP-co-AA) > Poly(NAP-co-AA)

> Poly(NAP-co-St)

The low Q value of NAP in copoly(NAP-co-AN) compared with that in others presumably results from the fact that the resonance stability of AN is greater than that of MMA or AA.

The copolymers obtained from the reaction of NAP with vinyl monomers were found to be better polymeric initiators than poly(NAP-co-St). It seems that their copolymers are close to the ideal random copolymer. This is consistent with the experimental data shown in the figures.

TABLE 1. Copolymerization of N-Acryloyl Pyrrolidone and Methyl Methacrylate in DMF at 65°C

Monomer charged in mole fraction		Conversion (%)	Copolymer composition mole fraction	
NAP	MMA		NAP	MMA
0.3	0.7	4.51	0.45	0.55
0.4	0.6	4.25	0.55	0.45
0.5	0.5	5.51	0.65	0.35
0.6	0.4	7.32	0.74	0.26
0.7	0.3	9.63	0.80	0.20

TABLE 2. Copolymerization of N-Acryloylpyrrolidone and Acrylamide in DMF at 65°C

Monomer charged in mole fraction		Conversion (%)	Copolymer composition mole fraction	
NAP	AA		NAP	AA
0.2	0.8	12.8	0.389	0.611
0.3	0.7	8.3	0.493	0.507
0.4	0.6	9.8	0.622	0.378
0.6	0.4	21.5	0.787	0.213
0.7	0.3	17.4	0.849	0.151

Effect of Variables on Grafting

Effect of Grafting Time

Figure 1 shows the effect of grafting time on the percent grafting. The formation of nylon-4 branches is initiated during the initial phase of the process (up to 30 min). After this time, growth of the initially formed nylon-4 branches appears to be the principal reaction.

Effect of KOH Concentration

The effect of KOH concentration on the percent grafting and viscosity of the graft copolymer is shown in Tables 5, 6, and 7 and Fig. 2. Maximum grafting was achieved when the KOH concentration was

TABLE 3. Copolymerization of N-Acryloylpyrrolidone and Acrylonitrile in DMF at 65° C

Monomer charged in mole fraction		Conversion (%)	Copolymer composition mole fraction	
NAP	AN		NAP	AN
0.2	0.8	0.8	0.358	0.662
0.3	0.7	9.6	0.454	0.546
0.5	0.5	10.9	0.642	0.358
0.6	0.4	10.1	0.722	0.278
0.7	0.3	12.9	0.796	0.204

TABLE 4. Parameters of Copolymerization

M_1	M_2	r_1	r_2	Q_1	e_1
NAP	MMA	1.83	0.53	1.30	0.25
NAP	AN	1.56	0.43	0.62	1.50
NAP	AA	1.76	0.48	1.85	0.51

TABLE 5.[a] Effect of KOH Concentration on % Grafting and Viscosity

Run no.	KOH concentration ($10^2 \times \underline{M}$)	Grafting (%)	Inherent viscosity
1	1	1053	0.92
2	2	2321	1.50
3	3	2782	1.83
4	5	2460	1.55

[a] Graft copolymerization of pyrrolidone onto poly(NAP-co-AN).

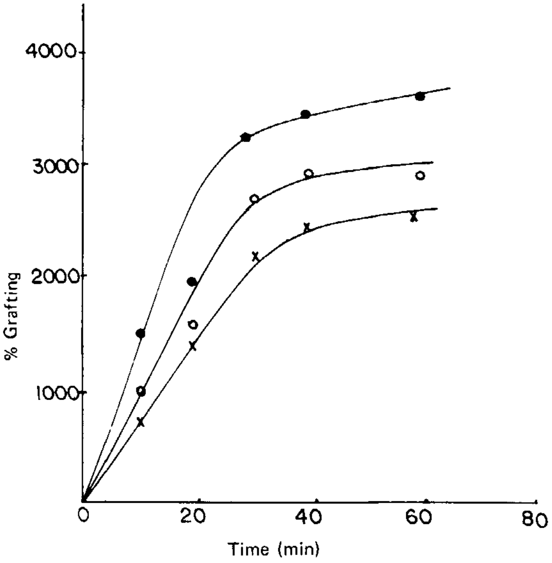

FIG. 1. Effect of grafting time on the graft copolymerization of 2-pyrrolidone. [Pyrrolidone] = 1 M. [Catalyst] = 0.03 M. Polymeric initiator: 1 g. Temperature: 50°C. (●) Poly(NAP-co-MMA). (○) Poly(NAP-co-AA). (X) Poly(NAP-co-AN). [NAP]/[vinyl monomers] = 1/10.

TABLE 6.[a] Effect of KOH Concentration on % Grafting and Viscosity

Run no.	KOH concentration ($10^2 \times$ M)	Grafting (%)	Inherent viscosity
1	1	1080	0.97
2	2	2131	1.34
3	3	3097	2.08
4	5	2761	1.82

[a] Graft copolymerization of pyrrolidone onto poly(NAP-co-AA).

TABLE 7.[a] Effect of KOH Concentration on % Grafting and Viscosity

Run no.	KOH Concentration ($10^2 \times \underline{M}$)	Grafting (%)	Inherent viscosity
1	1	1846	1.21
2	2	2630	1.78
3	3	3523	2.46
4	5	3196	2.17

[a] Graft copolymerization of pyrrolidone onto poly(NAP-co-MMA).

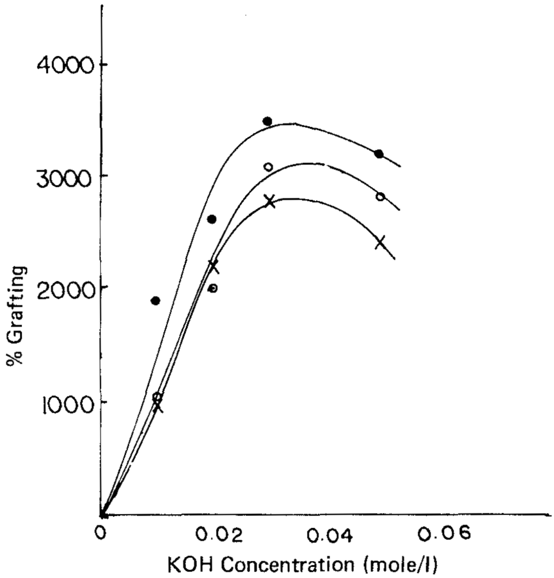

FIG. 2. Effect of KOH concentration on the graft copolymerization of 2-pyrrolidone. [Pyrrolidone] = 1 $\underline{M}$. Reaction time: 30 min. Temperature: 50°C. Polymeric initiator: 1.0 g. (●) Poly(NAP-co-MMA). (○) Poly(NAP-co-AA). (×) Poly(NAP-co-AN). [NAP]/[vinyl monomers] = 1/10.

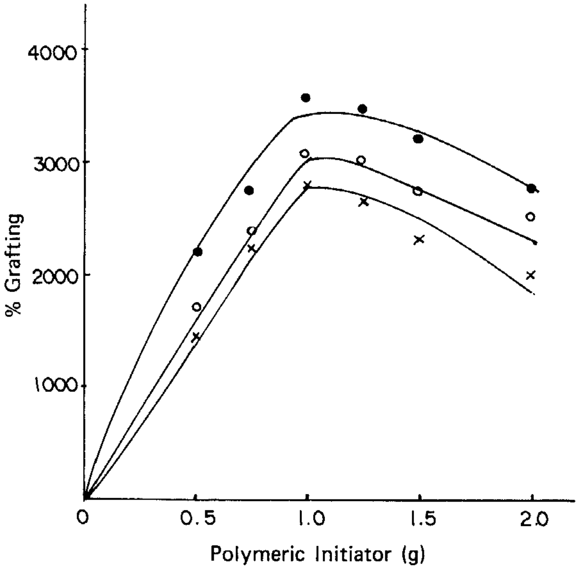

FIG. 3. Effect of the polymeric initiator on the graft copolymerization of 2-pyrrolidone. [Pyrrolidone] = 1 M. [Catalyst] = 0.03 M. Reaction time: 30 min. Temperature: 50°C. (●) Poly(NAP-co-MMA). (○) Poly(NAP-co-AA). (×) Poly(NAP-co-AN). [NAP]/[vinyl monomers] = 1/5.

0.03 M. The degree of grafting then decreased with an increasing concentration of KOH. The viscosity of the graft copolymer increases with KOH concentration up to 0.03 M and then decreases.

The rate of polymerization generally increases with an increasing concentration of KOH as a catalyst. When the relative concentration ratio of KOH to polymeric initiator is increased, however, the rate of graft copolymerization decreases and the percent grafting and the viscosity of the resulting copolymer is low.

This result is due to the depolymerization of graft copolymer as a side reaction and the homopolymerization of 2-pyrrolidone while the graft copolymerization is proceeding.

Effect of Polymeric Initiator

As shown in Fig. 3, the percent grafting increases with an increasing amount of copolymer up to 1.0 g and then decreases with a further increase of copolymer. This is attributed to the change in the relative ratio of copolymer with respect to the KOH concentration. The percent grafting of poly(NAP-co-MMA) is higher than of other copolymers. This may be because poly(NAP-co-MMA) contains the most randomly distributed N-acyllactam groups.

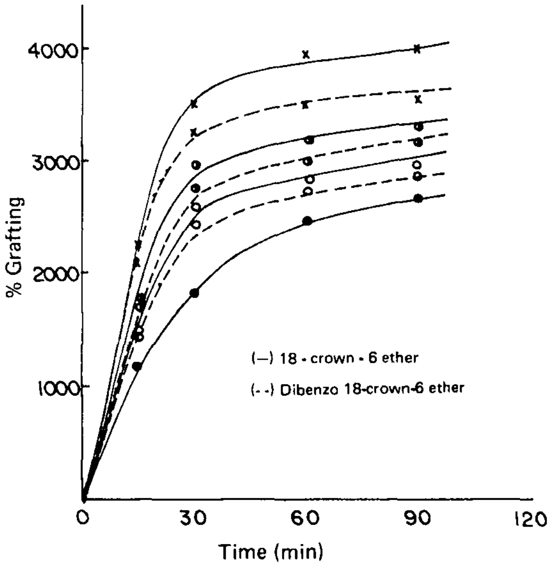

FIG. 4. Effect of the crown ether concentration on the graft copolymerization of 2-pyrrolidone. [Pyrrolidone] = 1 M. [Catalyst] = 0.03 M. Temperature: 50°C. Polymeric initiator: Poly(NAP-co-AA), 1.0 g. [NAP]/[AA] = 1/5. (●) Nil. (○) [Crown ether]/[catalyst] = 0.3. (◑) [Crown ether]/[catalyst] = 0.5. (×) [Crown ether]/[catalyst] = 1.0.

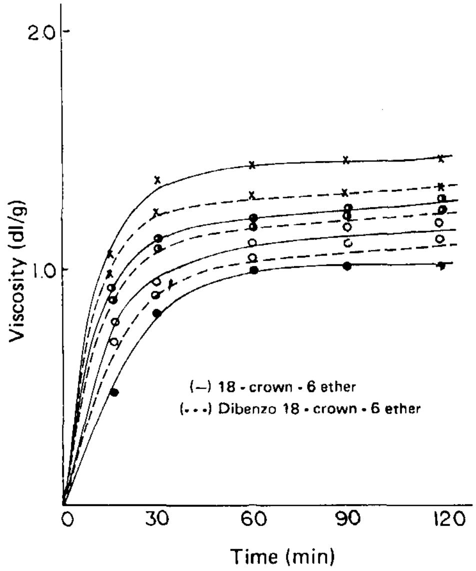

FIG. 5. Effect of the crown ether concentration on the graft copolymer viscosity. [Pyrrolidone] = 1 M. [Catalyst] = 0.03 M. Temperature: 50°C. Polymeric initiator: Poly(NAP-co-AA), 1.0 g. [NAP]/[AA] = 1/10. (●) Nil. (○) [Crown ether]/[catalyst] = 0.3. (◐) [Crown ether]/[catalyst] = 0.5. (×) [Crown ether]/[(catalyst] = 1.0.

Effect of the Crown Ether on Grafting

It has been reported that the 18-crown-6 ether, dibenzo 18-crown-6 ether, and cryptates affect the anionic ring-opening polymerization of cyclic lactams [8, 9]. Figures 4 and 5 show the effect of the concentration of crown ether on the percent grafting and the viscosity of the graft copolymer. One notes that the percent grafting and the viscosity of graft copolymer increases with an increasing concentration of crown ether. This results from the increase of nucleophilicity of potassium pyrrolidone salt as a catalyst and the acceleration of the initial rate of graft copolymerization by the addition of crown ether. The effect of 18-crown-6 ether on grafting yield was higher than that of dibenzo 18-crown-6. This is due to the poor solubility of dibenzo 18-crown-6 in pyrrolidone compared to that of 18-crown-6 ether.

REFERENCES

[1] R. J. Ceresa, Block and Graft Copolymers, Wiley, New York, 1973.

[2] A. Gasperowicz and W. Laskawski, J. Polym. Sci., Polym. Chem. Ed., 16, 49 (1978).

[3] O. Wichterle and V. Gregor, J. Polym. Sci., 34, 309 (1959).
[4] Y. Nitadori, P. Rempp, and E. Franta, Makromol. Chem., 179, 941 (1978).
[5] G. S. Sur, B. Jung, and S. K. Choi, J. Korean Chem. Soc., 20, 525 (1976).
[6] G. S. Sur and S. K. Choi, Ibid., 21, 160 (1977).
[7] G. S. Sur, S. K. Noh, and S. K. Choi, J. Polym. Sci., Polym. Chem. Ed., 19, 223 (1981).
[8] A. Deffieux and S. Boileau, Macromolecules, 9, 369 (1976).
[9] J. M. Lehn, Struct. Bonding (Berlin), 16, 1 (1973).
[10] C. J. Pedersen, J. Am. Chem. Soc., 89, 7017 (1967).

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