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Radical Polymerization of Methacrylic Acid in the Presence of Copolymers of 4-Vinylpyridine in Methanol

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SUMMARY

Random copolymers of 4-vinylpyridine(4VP) with styrene and with acrylamide were effective to enhance the overall rate of radical polymerization of methacrylic acid(MA) in methanol. The rate maximum did not occur at the equimolar ratio of 4VP unit/MA but it depended on the copolymer composition.

INTRODUCTION

Both enhanced rate of polymerization and the production of larger molecular weight were observed when methacrylic acid(MA) was polymerized in the presence of poly(4-vinylpyridine) with a radical(FUJIMORI,1979). Similar results were reported for acrylic acid(FERGUSON and SHAH,1968) and MA(ENDO et al,1971) that showed rate enhancement in the presence of interacting polymers,the rate maximum appearing at close to 1:1 monomer:polymer repeating unit ratio. The "zipping-up" mechanism for the propagation of the complexed monomer molecules along the template polymer was proposed by these authors in order to account for the maximum of the enhanced rate of polymerization.

Since the template model requires a long sequence of interacting units on the template(KÄMMERER and OZAKI,1966), it is interesting to examine the effect of discontinuous and random location of interacting units on the chain of added copolymers. Copolymer of 4-vinylpyridine(4VP) was used in this experiment to see the effect of the added copolymers on the rate of polymerization of MA.

EXPERIMENTAL

Reagent grade MA(Tokyo Kasei),4VP(T.K.),styrene(ST)(British Drug House) and the solvents were fractionally distilled before use. 2,2'-Azobisisobutyronitrile(AIBN)(B.D.H.) was recrystallized from methanol. Reagent grade acrylamide(AM)(B.D.H.) was used as received.

The copolymers of 4VP were prepared with AIBN in $CHCl_3$ or in N,N'-dimethylformamide solution followed by the Soxhlet extraction with diethyl ether for 4 days. The overall composition of 4VP copolymers was determined by the potentiometric titration of the pyridinium chloride group with 0.025 M $AgNO_3$ with Ag/AgCl electrodes: The copolymers were dissolved in methanol and an excess amount of conc. HCl was added to quarternize the 4VP units. The polymer was precipitated in acetone and purified by reprecipitation. Poly(4VP-co-ST)(a) with the mole fraction of 4VP unit in the copolymer,x_{4VP}=0.783, poly(4VP-

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co-ST) (b), x_{4VP}=0.642, and poly(4VP-co-AM), x_{4VP}=0.638, were prepared.

Polymerization of MA was carried out in methanol in degassed glass ampules and the rate of polymerization was measured gravimetrically by subtracting the weight of added polymer from that of total polymer precipitated in diethyl ether. Ubbelohde type viscometers and Perkin-Elmer IR spectrophotometer Type 597 were used.

RESULTS AND DISCUSSION

The reduced viscosity of copolymers in methanol was measured by successively diluting with methanol solution of MA. The plot of the reduced viscosity with respect to the concentration of the polymer showed a break when the mole ratio of MA in the solution and the 4VP units in the copolymer was close to 1:1. This suggests a 1:1 stoichiometry in the hydrogen bonded complexation between the acid group of MA and the pyridine nitrogen of the coplymer.

Fig.1. Reduced viscosity(η_{red}) of copolymers in MA/methanol solution at 25°C. The vertical lines show the mole ratio of 4VP unit/MA in solution.
(▲) Poly(4VP-co-AM) x_{4VP}=0.638
(●) Poly(4VP-co-ST) (a) x_{4VP}=0.783

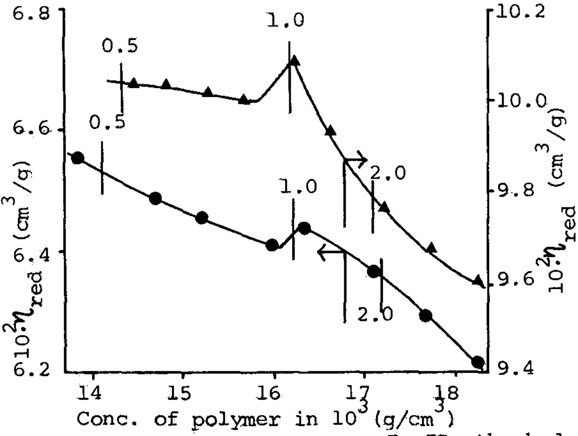
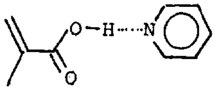
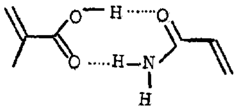


TABLE 1.

The IR absorption of bonded O-H of MA in CCl_4.

Mole fraction of MA	With pyridine [MA+Py]=1.20M	With acrylamide [MA+AM]=0.68 M
1.0	2615 cm^{-1}	
0.9	2605 cm^{-1}	2610 cm^{-1}
0.8	2600	2590
0.7	2590	2585
0.6	2570	2580
0.5	2550	2575
0.4	2540	2567
0.3	2540	2560
0.2	2540	2555
0.1	2540	2550
0	--	--
	$\Delta\nu OH \cong 75$ cm^{-1}	$\Delta\nu OH \cong 65$ cm^{-1}

In IR, the hydrogen bonded O-H of MA absorbs at 2615 cm^{-1} in CCl_4 solution at room temperature. The absorption shifts gradually to a lower wavenumber as a base is added under the condition that the total concentration of the base and MA is kept constant. Although the interaction between the amide group of poly(4VP-co-AM) and MA in methanol was not apparent in the viscosity measurement, the IR absorption of the hydrogen bonded O-H of MA shifts by 65 cm^{-1} in CCl_4 when bonded to AM as shown in TABLE 1. A stronger hydrogen bonding between pyridine and MA is apparent by the larger shift of the absorption toward the lower energy direction.

The effect of added 4VP copolymers on the rate of the polymerization of MA is shown in Fig.2. Contrary to the template model, the copolymers of 4VP were effective in enhancing the overall rate. According to the "zipping-up" model, the complexed monomer molecules are consecutively located on a polymer template. Disruption of the sequence of 4VP units along the template would not be favorable for the swift propagation. The rate maxima did not coincide with the equimolar 4VP unit:MA ratio. With the poly(4VP-co-AM), the rate maximum was close to 4VP unit:MA molar ratio of 0.5, which corresponded to the overall molar ratio of (4VP+AM) units:MA of about 0.8.

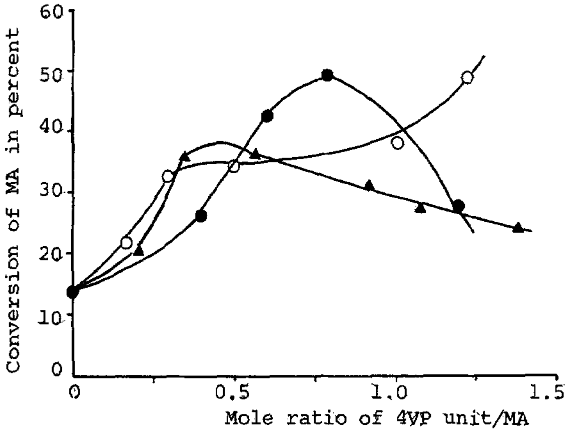


Fig.2. Conversion vs. mole ratio of 4VP unit/MA. [MA]=0.369 mol/dm^3, [AIBN]=1.77x10^{-2} mol/dm^3, in methanol at 60°C, 1.0 hour.
(▲) Poly(4VP-co-AM) x_{4VP}=0.638,
(●) Poly(4VP-co-ST)(a) x_{4VP}=0.783,
(○) Poly(4VP-co-ST)(b) x_{4VP}=0.642.

It is considered that the balance of the propagation rate and the termination rate decide the overall rate of the polymerization when the growing polymer radical is complexed to the added polymer chain or to the polymer matrix. When the hydrogen-bond complexation is not complete, the complexed growing polymer radical may encounter a free monomer molecule that penetrates into the polymer matrix, and also it may encounter a complexed monomer molecule owing to the kinetical movement of the added polymer chain segments. It is possible that the sluggishness of the complexed polymer radicals retards the termination and enhances both the overall rate and the average molecular weight. When the concentration of the interacting polymer site is in excess, the propagation has to solely rely on the kinetical movement of the added polymer segments as most of the monomer molecules are complexed in the polymer matrix, while the requirement for the termination is not so much altered. This may result in the slower overall rate. This balance may be affected by the conformation of the polymer, the sequence distribution of the interacting sites, and the polarity of the comonomer units.

REFERENCES

ENDO,T.,NUMAZAWA,R. and OKAMURA,M.:Kobunshi Kagaku 28,541(1971)
FERGUSON,J. and SHAH,S.A.O.:Eur. Polym. J. 4,343(1968)
FUJIMORI,K.:Makromol. Chem. 180,1743(1979)
KÄMMERER,H. and OZAKI,S.:Makromol. Chem. 91,1(1966)

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