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MATRIX POLYMERIZATION OF ACRYLAMIDE INDUCED BY THE INTERACTION BETWEEN CARBONYL AND AMIDE GROUPS

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ABSTRACT

Polymerizations of acrylamide (AAm) in the presence of several homo- and copolymers such as poly(methyl vinyl ketone) (poly-MVK) and poly(*N*-vinylpyrrolidone) (poly-VPr), copoly(MVK–St), and copoly(VPr–St) were carried out in tetrahydrofuran (THF) at 30°C without catalyst. Similarly, the polymerizations of AAm in the presence of poly(methyl methacrylate) were also carried out in THF at 40°C. The increasing concentration of these matrix polymers increased the polymerizability of AAm. Number-average molecular weight ($\overline{M}_n$) of the resulting poly-AAm were close to the molecular weight ($\overline{M}_n$) of the matrix polymers. The polymerizability of *N*-methylacrylamide was lower than that of AAm, and *N,N*-dimethylacrylamide did not polymerize at all. From these results it appeared that these matrix polymerizations proceeded by the interaction between the carbonyl group in the matrix polymer and the amide group of the AAm monomer.

INTRODUCTION

In an earlier article [1] we reported on the copolymerizability of methyl vinyl ketone (MVK, M_1) with acrylamide (AAm, M_2) without catalyst. This uncatalyzed copolymerization proceeded easily in tetrahydrofuran (THF) below room temperature. Under several conditions of light, the monomer reactivity ratios were obtained as follows: $r_1 = 0.70$ and $r_2 = 0.79$ for irradiation under room light; $r_1 = 0.78$ and $r_2 = 0.97$ in the absence of light; $r_1 = 1.28$ and $r_2 = 1.23$ for irradiation with UV light. The presence of oxygen gas in the copolymerization system tends to decrease the rate of copolymerization (R_p). The overall activation energy was obtained from Arrhenius plots and was found to be 19.7 kcal/mol, which suggests a mechanism of free-radical polymerization. Meanwhile, it is interesting that R_p in unirradiated systems had a higher value than in the irradiated system with room light or UV light. These R_p attained maximum values at about 50 mol% in monomer feed, and neither monomer homopolymerized. From these phenomena we deduced the presence of an interaction between carbonyl group and amide group.

We also reported on the matrix polymerizations of acrolein and MVK in the presence of poly-AAm and poly(*N*-vinylpyrrolidone) induced by imidazole catalyst [2]. This phenomena also supports the above-mentioned idea based on the interaction between monomer and polymer.

In this present paper we report on the matrix polymerizability of AAm in the presence of several homopolymers such as poly-MVK, poly(*N*-vinylpyrrolidone) (poly-VPr), and poly(methyl methacrylate) (poly-MMA), and copolymers such as copoly(MVK–styrene) and copoly(VPr–styrene).

EXPERIMENTAL

Materials

All monomers such as methyl vinyl ketone (MVK), acrylamide (AAm), *N*-vinylpyrrolidone (VPr), methyl methacrylate (MMA), *N*-methylacrylamide, and *N,N*-dimethylacrylamide, and tetrahydrofuran (THF) and other solvents were prepared as described previously [1–4].

The Synthesis of Matrix Polymers

The matrix polymers such as poly-MVK, poly-VPr, and poly-MMA were synthesized by radical-initiated polymerization.

In order to obtain the poly-MVK, the radical homopolymerization of MVK was carried out in benzene at 60°C using 2,2′-azobisisobutyronitrile (AIBN) as a radical initiator: polymerization time, 15 hours; conversion, 74.9% M_n, 87.2 ×

10^3. The radical copolymerizations of MVK with St were carried out in benzene at 60°C; incorporated ratios of MVK in the copolymer were 100, 80, and 50 mol%.

The poly-VPr and copoly(VPr–St) were also synthesized in benzene at 60°C by use of AIBN: polymerization time, 17 hours; conversion, 94.7%; $\overline{M}_n$, 102.3×10^3 for poly-VPr; and polymerization time, 32 hours; incorporated ratios of VPr in the copolymer were 90, 50, 40, and 30 mol%.

The radical polymerizations of MMA were carried out in benzene at 60°C using AIBN: polymerization time, 15 hours; conversion, 74.1%; $\overline{M}_n$, 46.5×10^3.

The Method of Matrix Polymerization

The matrix polymerizations of AAm were carried out heterogeneously in THF at room temperature (30 or 40°C) under an argon atmosphere according to the method given in a previous paper [1]. THF solutions containing the required amounts of AAm and the matrix polymers were placed in the main and side arms of the polymerization tube, respectively. The tube was placed in a thermostat kept at 30 or 40°C, and both solutions were mixed to start the matrix polymerization reaction.

During the course of the polymerization, THF-insoluble poly-AAm precipitated. After the polymerization time described in the text, the resulting poly-AAm was filtered, dried in vacuo, and weighed to determine the yield. The filtrate was poured into a large amount of methanol, and the matrix polymer of poly-MVK or poly-MMA was filtered off. The matrix polymer of poly-VPr was filtered from a large amount of diethyl ether.

Determination of Polymerization Rate (R_p) of AAm

The R_p of AAm was determined from the time–conversation curve of the polymerization reaction of AAm [1]. The consumption of AAm was traced by HPLC.

Analyses

Infrared (IR) spectra of a KBr disk or film were recorded with a Perkin-Elmer 1760 FT-IR. The molecular weight distributions of the polymers were estimated by gel permeation chromatography (GPC) with an Hitachi D-2520 integrator, L-5030 column oven, L-3350 RI monitor, L-6000 pump, GL-A160 column, and W-550 column.

RESULTS AND DISCUSSION

Polymerizations of AAm in the Presence of Poly-MVK and Copoly(MVK–St) without Catalyst

The polymerizations of AAm in the presence of poly-MVK were carried out in THF at 30°C under an argon atmosphere without catalyst (Table 1). The AAm did not polymerize without poly-MVK. The increasing concentration of poly-MVK

TABLE 1. Polymerization[a] of AAm in the Presence of Poly-MVK and GPC Data

Poly-MVK,[b] g	Conversion, %	$\overline{M}_n \times 10^{-3}$	$\overline{P}_n \times 10^{-2}$
0	0	–	–
0.05	26.2	92	13
0.10	28.1	91	13
0.15	28.1	92	13
0.20	36.1	93	13

[a] Polymerization conditions: Total volume, 20 mL; [AAm] = 0.3 mol/L; polymerization time, 140 hours; solvent, THF; temperature, 30°C.

[b] $\overline{M}_n = 87 \times 10^{-3}$; $\overline{P}_n = 13 \times 10^{-2}$.

increased the conversion of the resulting poly-AAm, and the $\overline{P}_n$ (13×10^2) of poly-MVK was in good agreement with the $\overline{P}_n$ (13×10^2) of the resulting poly-AAm.

The result of the polymerizations of AAm in the presence of copoly(MVK-St) is given in Figs. 1 and 2. The increasing concentration of copoly(MVK-St) increased the polymerization rate (R_p) of AAm. However, the decreasing content of MVK in copoly(MVK-St) decreased markedly the polymerizability of AAm.

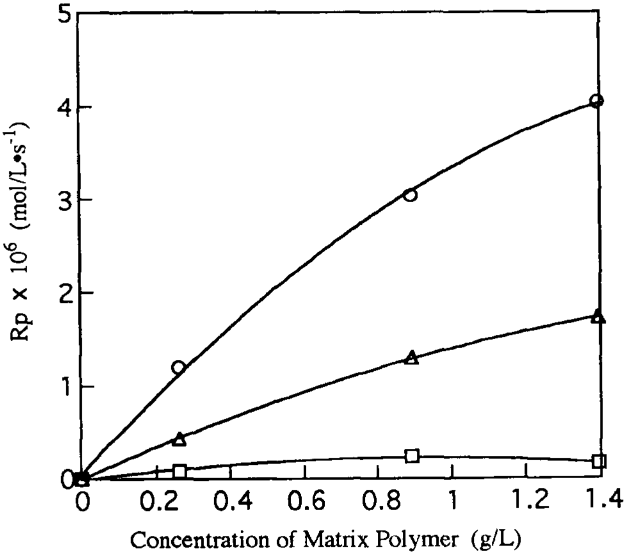


FIG. 1. Relationships between concentration of matrix polymer and R_p of AAm. Homopolymer of MVK (○); copolymer [MVK 80:St 20] (△); [MVK 50:St 50] (□); [AAm], 0.6 mol/L; polymerization time, 19.5 hours; solvent, THF; temperature, 30°C; atmosphere, Ar gas.

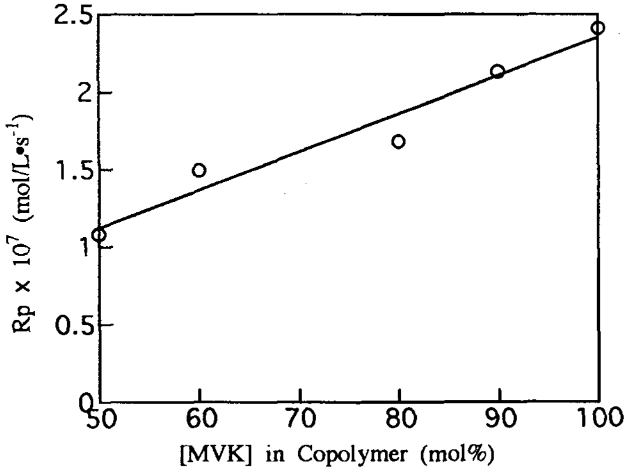


FIG. 2. Relationship between MVK content in copoly(MVK-St) and R_p of AAm.

In order to investigate the relation between the structure of the amide monomer and its polymerizability, the uncatalyzed polymerizations of AAm and several AAm derivatives were also carried out in the presence of poly-MVK and copoly(MVK-St) in THF at 30°C under argon (Table 2). The polymerizability of *N*-methylacrylamide (MAAm) was lower than that of AAm, and *N*,*N*-dimethylacrylamide (DMAAm) did not polymerize at all in these polymerization conditions. These results indicates that the presence of free N—H in the amide group is important for the interaction between the matrix polymer and AAm.

It is interesting that DMAAm does not polymerize in this matrix system although both AAm ($Q = 0.52$, $e = 1.15$) and DMAAm ($Q + 0.41$, $e = -0.26$) easily polymerize under usual radical polymerization conditions. The low concentration of the radical initiator in the matrix system seems to be one reason for this

TABLE 2. Polymerization[a] of AAm and Its Derivatives in the Presence of Poly-MVK or Copoly(MVK-St)

AAm, mol/L	MAAm, mol/L	DMAAm, mol/L	Polymerization time, h	Conversion, %	$R_p \times 10^5$, mol/(L·s)
0.3[b]	–	–	18.8	16.4	7.25
0.3[c]	–	–	91.0	11.7	1.07
–	0.3[b]	–	18.5	2.6	0.77
–	0.3[c]	–	234.8	3.5	0.08
–	–	0.3[b]	240.0	0	–
–	–	0.3[c]	240.0	0	–

[a] Polymerization conditions: solvent, THF; temperature, 30°C.
[b] Homopolymer of MVK; 2.1 g/L.
[c] Copolymer compositions: MVK:St = 60:40; 2.1 g/L.

TABLE 3. Polymerization[a] of AAm in the Presence of Poly-VPr and GPC Data

Poly-VPr,[b] g	Conversion, %	$\overline{M}_n \times 10^{-3}$	$\overline{P}_n \times 10^{-2}$
0	0	–	–
0.025	28.2	68	10
0.050	32.9	67	10
0.075	44.6	66	9
0.100	54.0	63	9

[a] Polymerization conditions: total volume, 20 mL; [AAm] = 0.3 mol/L; polymerization time, 110 hours; solvent, THF; temperature, 30°C.

[b] $\overline{M}_n = 102 \times 10^3$; $\overline{P}_n = 9 \times 10^2$.

difference. The result described above, however, strongly indicates that the interaction, probably the hydrogen bonding interaction, between the carbonyl group in the matrix polymer and the amide N—H of acrylamides (AAm and MAAm) is an essential factor in this polymerization reaction. That is, the monomers line up on the matrix polymer with the carbonyl-amide interaction, and this organization lowers the activation energy of the reaction system and induces polymerization even though the concentration of initiators is rather low.

Polymerizations of AAm in the Presence of Poly-VPr and Copoly(VPr–St) without Catalyst

In a similar manner as above, the polymerizability of AAm was investigated in THF at 30°C using poly-VPr and copoly(VPr-St) as the matrix polymers (Tables 3 and 4). In these runs the increasing concentration of poly-VPr and copoly(VPr–

TABLE 4. Polymerization[a] of AAm in the Presence of Copoly(VPr–St)

Copoly(VPr–St)		Conversion,	$R_p \times 10^7$,
VPr, mol%	St, mol%	%	mol/(L·s)
100	0[b]	28.4	5.145
70	30	23.5	4.270
50	50	17.2	3.132
40	60	14.6	2.645
30	70	7.5	1.368
–	–	0	0

[a] Polymerization conditions: total volume, 20 mL; [AAm] = 0.3 mol/L; polymerization time, 46 hours; solvent, THF; temperature, 30°C.

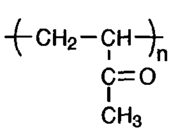
[b] Homopolymer of VPr was used as a matrix polymer.

St) increased the conversion to poly-AAm. $\overline{M}_n$ and ($\overline{P}_n$) of poly-AAm were in agreement with poly-VPr as a matrix polymer (Table 3). And the increasing content of VPr in copoly(VPr–St) increased the polymerizability of AAm (Table 4).

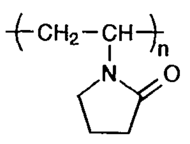
The Polymerization of AAm in the Presence of Poly-MMA

We also tried to investigate the polymerizability of AAm induced by poly-MMA. The polymerization results are given in Table 5. The polymerizations were carried out in THF at 40°C. AAm did not polymerize without poly-MMA in these polymerization conditions. The increasing concentration of poly-MMA also increased the conversion of the resulting poly-AAm. And the $\overline{P}_n$ (6×10^2) of the resulting poly-AAm agreed roughly with the $\overline{P}_n$ (8 or 9×10^2) of poly-MMA as a matrix polymer.

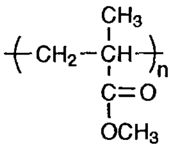
In this study, the following matrix polymers containing carbonyl group in the side chain were used:



Poly(methyl vinyl ketone)



Poly(*N*-vinylpyrrolidone)



Poly(methyl methacrylate)

Among them, poly-MMA seems to be most effective as the matrix polymer, and poly-VPr seems more effective than poly-MVK. This order probably reflects the efficiency of the interaction between the C=O group in the matrix polymer and the amide N—H in AAm. The interaction efficiency is concerned with the electron density on the O-atom of the C=O group in the matrix polymer and the steric hindrance around the interaction point. The latter factor, the steric factor, was

TABLE 5. Polymerization[a] of AAm in the Presence of Poly-MMA and GPC Data

Poly-MMa,[b] g	Conversion, %	$\overline{M}_n \times 10^{-3}$	$\overline{P}_n \times 10^{-2}$
0	0	—	—
0.05	31.1	67	9
0.10	43.4	65	9
0.15	83.6	59	8
0.20	87.9	57	8

[a] Polymerization conditions: total volume, 20 mL; [AAm] = 0.3 mol/L; polymerization time, 140 hours; solvent, THF; temperature, 40°C.

[b] $M_3 = 47 \times 10^3$; $P_n = 6 \times 10^2$.

clearly demonstrated by a comparison of poly-MMA and poly(methylacrylate) (poly-MA) as matrix polymers. That is, poly-MA also induced the polymerization of AAm, and showed higher polymerizability than poly-MMA.

We reported [1] that the matrix polymerization of AAm in the presence of poly-MVK proceeded by a free-radical polymerization mechanism. The fact that the addition of 1,1-diphenyl-2-picrylhydrazil as a radical inhibitor retarded the polymerization strongly supported this mechanism. The radical source in the initiation step is not clear, but it is well known that poly-MVK decomposes upon irradiation with UV light because poly-MVK has an n-π^* absorption band (330–360 nm) associated with the carbonyl group as in the Norrish reaction [5]. In this present study, however, the molecular weights of the matrix polymers recovered after the polymerization reaction did not decrease. Therefore, the radical seems to be generated by homolysis on the side chain of poly-MVK.

Matrix polymerizations of AAm in the presence of poly-VPr or poly-MMA were also observed. In analogy with poly-MVK, there is some possibility of a radical mechanism based on the decomposition of poly-VPr and poly-MMA. The mechanism of these polymerizations is not clear at present, but it was clarified that the organization of the monomers on the matrix polymer based on carbonyl–amide interaction induced these polymerizations.

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