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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Hydrogen Transfer Polymerization Mechanism of Acrylamide Induced by Propagating Polyacrolein Anion

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**To cite this Article** Yamashita, Natsuki , Ikezawa, Kazuyuki , Yamamoto, Yasuhiro , Kinugasa, Hirofumi and Maeshima, Toshihisa(1984) 'Hydrogen Transfer Polymerization Mechanism of Acrylamide Induced by Propagating Polyacrolein Anion', *Journal of Macromolecular Science, Part A*, 21: 3, 291 – 300

**To link to this Article:** DOI: 10.1080/00222338408069463

**URL:** <http://dx.doi.org/10.1080/00222338408069463>

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## Hydrogen Transfer Polymerization Mechanism of Acrylamide Induced by Propagating Polyacrolein Anion

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### ABSTRACT

In order to investigate the interaction between acrolein (AL) and acrylamide (AAM) on anionic copolymerization, the homopolymerizabilities of AL in the presence of several *p*-substituted phenylacetamides such as *p*-nitroacetanilide, *p*-chloroacetanilide, acetanilide, and *p*-methylacetanilide were investigated in tetrahydrofuran at 0°C using imidazole as an anionic catalyst. A linear correlation was obtained by Hammett's equation as described by  $\log R_p/R_{p_0} = 0.28\sigma$ . This result suggests that the homopolymerizability of AL is influenced by the structure of the amide compound. An increase of the additive propionamide (PAM) on the homopolymerization of AL induced by the pyridine-water initiation system increased the polymerization rate  $R_p$ ; however, it decreased the intrinsic viscosity  $[\eta]$  of poly-AL. From the measurement of infrared spectroscopy and elementary analysis, the presence of a chain transfer reaction between the poly-AL anion and PAM was found.

These results support the presence of interaction between AL and AAm derivatives in the copolymerization system.

## INTRODUCTION

In a previous article [1] we reported that acrolein (AL) can be polymerized readily by imidazole (Im) below room temperature. Other polar vinyl monomers, such as methyl vinyl ketone, methyl methacrylate, and acrylamide (AAm), polymerize in a similar manner [2]. On the other hand, in the anionic copolymerization of AL with AAm in the presence of Im, it is interesting to note that the structure of the AAm unit in the copolymer is due to both polymer units and depends on vinyl polymerization and hydrogen transfer polymerization [3]. In order to investigate this polymerization mechanism, the anionic copolymerization of AL with methacrylamide (MAAm) was carried out in THF at 0°C using Im as the catalyst [4]. In this investigation, hydrogen transfer polymerization was not observed. However, it became clear that there was interaction between polyacrolein anions and the amide groups in AAm or MAAm.

We report the results of some investigations on these interactions and discuss them in this paper.

## EXPERIMENTAL

### Materials

AL, pyridine (Py), and THF were prepared in the manner described in a previous article [1]. All the amide compounds, such as propionamide (PAm), acetamide (AcAm), and N-methylacetamide (MAcAm), were purified by distillation or recrystallization in the usual way. p-Substituted phenylacetamides, such as p-nitroacetanilide, acetanilide, and p-methylacetanilide, were also purified in the usual way.

### Polymerization Method

In accord with a previous paper [1], the anionic polymerizations were carried out in THF at 0°C under nitrogen atmosphere. The required amounts of catalysts and solvent were placed into a tube. Then a fixed amount of monomer was added to start the polymerization reaction. Polymerization was stopped in a large amount of ether containing hydrochloride, and the precipitate was filtered to dryness.

### Kinetics

The initial polymerization rate  $R_p$  was estimated from the decreasing amount of monomer by means of gas chromatography. A straight-line relationship between the reaction time and the consumption of monomer was observed in the initial step of the reaction.

### Viscosity of Polymer

The viscosity of polymer was measured in methanol at 30°C with an Ostwald viscometer. The intrinsic viscosity  $[\eta]$  was determined from the specific viscosity  $\eta_{sp}/c$ .

### Analyses

Elementary analysis of polymers was estimated with a Yanagimoto CHN Corder MT-2. IR spectra of all polymers were taken in KBr on a Nihonbunkou IRA-1 spectrophotometer. The absorption band (1530  $\text{cm}^{-1}$ ) depending on the amide II group in polymer was estimated by an absorbance ratio method.

## RESULT AND DISCUSSION

### Additive Effect of Amide Compound

In a previous report [4] we obtained some interesting information through a detailed examination of the homopolymerizability of AL in the presence of several amide compounds (AcAm, MAcAm, and DMAcAm) induced by Im (Table 1).  $R_p$  in the presence of Py and methyl ethyl ketone increased slightly, but the presence of AcAm increased the polymerization rate of AL remarkably. In addition, the polymerizability is independent of the  $pK_a$  of the amide compounds.

### Additive Effect of p-Substituted Acetamide

In order to examine this, the homopolymerizations of AL in the presence of p-substituted phenylacetamide were carried out in THF at 0°C using Im as the catalyst. From this result a linear correlation was obtained from Hammett's equation as described by  $\log R_p/R_{p0} =$

TABLE 1. Additive Effect of Amide Compounds in the Polymerization of AL<sup>a</sup>

Additive	$R_p \times 10^5$ mol/L·min	$R_p/R_{p_0}$
-	5.4	1
Pyridine	5.9	1.1
Methyl ethyl ketone	7.1	1.3
Acetamide	13.4	2.5
N-Methylacetamide	9.6	1.8
N,N-Dimethylacetamide	2.2	0.4

<sup>a</sup>Polymerization conditions: Im concentration,  $5.15 \times 10^{-2}$  mol/L; additive concentration,  $2.17 \times 10^{-1}$  mol/L; solvent, THF; 0°C; atmosphere, nitrogen gas.

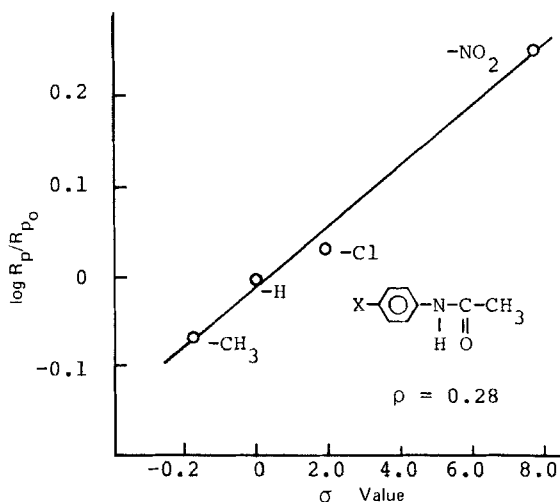
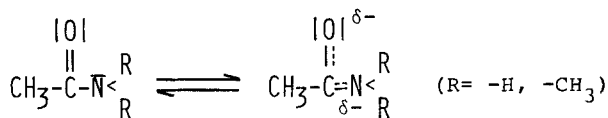


FIG. 1. Relation between  $\log R_p/R_{p_0}$  and Hammett's  $\sigma$  value. Polymerization conditions: Im concentration, 0.093 mol/L; AL concentration, 1.85 mol/L; additive concentration, 0.1 mol/L; solvent, THF; 0°C; atmosphere, nitrogen gas.

0.28 $\sigma$  (Fig. 1). This observation suggests that the polymerizability of AL is influenced by the structure of the amide compound. As a rule, the resonance structure of amide compound is



In this case the basicity is in the order DMAcAm > MAcAm > AcAm. In this work the presence of AcAm increased the  $R_p$  of AL remarkably. These results support the presence of interaction between AL and AAm and its derivatives in the copolymerization system.

### Polymerization of AL in the Presence of PAM

Homopolymerizations of AL in the presence of PAM were carried out in THF at 0°C using a Py and water mixture as the catalyst system [5] based on the above information. The relationship between  $R_p$  and the PAM concentration is shown in Fig. 2. An increase of PAM concentration increased  $R_p$ . This phenomenon was similar to that described

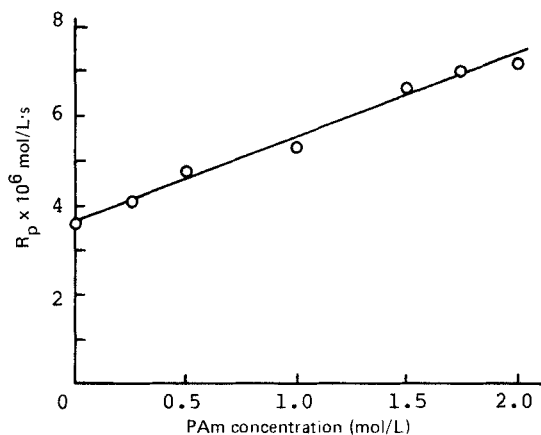


FIG. 2. Relation between PAM concentration and polymerization rate  $R_p$ . Polymerization conditions: Py concentration, 4.95 mol/L; water, 4.17 mol/L; total volume, 20 mL; solvent, THF; 0°C; atmosphere, nitrogen gas.

TABLE 2. Polymerization<sup>a</sup> of AL in the Presence of PAm Induced by the Py-Water Initiation System and Elementary Analysis of Poly-AL

Additive PAm (mol/L)	Polymerization time (h)	Conversion (%)	Nitrogen content (%)
0	44.7	38.3	0
0.25	44.5	42.5	1.72
0.50	44.0	48.8	2.09
1.00	25.7	31.7	2.46
1.50	20.2	31.1	2.91
1.75	20.0	32.6	3.17
2.00	19.8	33.1	3.55

<sup>a</sup>Py concentration, 4.95 mol/L; water concentration, 4.17 mol/L; AL concentration, 1.54 mol/L; solvent, THF; total volume, 20 mL; 0°C; atmosphere, nitrogen gas.

for other additives. The nitrogen content increased with PAm (Table 2). These nitrogen contents increased with an increase in PAm concentration. These results suggest that PAm added to the end of the polymer chain.

In order to investigate the structure of these polymers, the IR spectra were observed by the KBr disk method (Fig. 3). The IR spectrum of a poly-AL obtained by the Py-water system as an anionic initiator is shown in spectrum a. This spectrum has several characteristic absorption bands of poly-AL [5] such as those depending on the  $-\text{CH}_2-$  chain ( $3000\text{--}2900\text{ cm}^{-1}$ ) and on the  $=\text{C}=\text{O}$  group ( $1720\text{--}1680\text{ cm}^{-1}$ ). Spectrum b, for a radical copolymer of AL with AAm, shows an absorption band depending on the  $-\text{CONH}_2$  (amide I) group of the AAm unit ( $1660\text{ cm}^{-1}$ ). In spectrum c for an anionic copolymer [3] by the Py-water system, two absorption bands depending on  $-\text{CONH}_2-$  (amide I) and  $-\text{CONH}-$  (amide II) groups were observed at  $1660$  and  $1530\text{ cm}^{-1}$ , respectively. This latter absorption band, which depends on amide II, describes the presence of hydrogen transfer polymerization of the AAm monomer. On the other hand, in spectrum d the presence of absorption bands depending on  $-\text{CONH}_2$  (amide I) and  $-\text{CONH}-$  (amide II) groups were also observed at  $1530\text{--}1520\text{ cm}^{-1}$ . In spectrum e for poly-AL obtained in the presence of AcAm, however, the absorption bands depending on these amide groups were not observed. These observations clearly suggest the presence of a chain transfer reaction between the poly-AL anion and PAm.

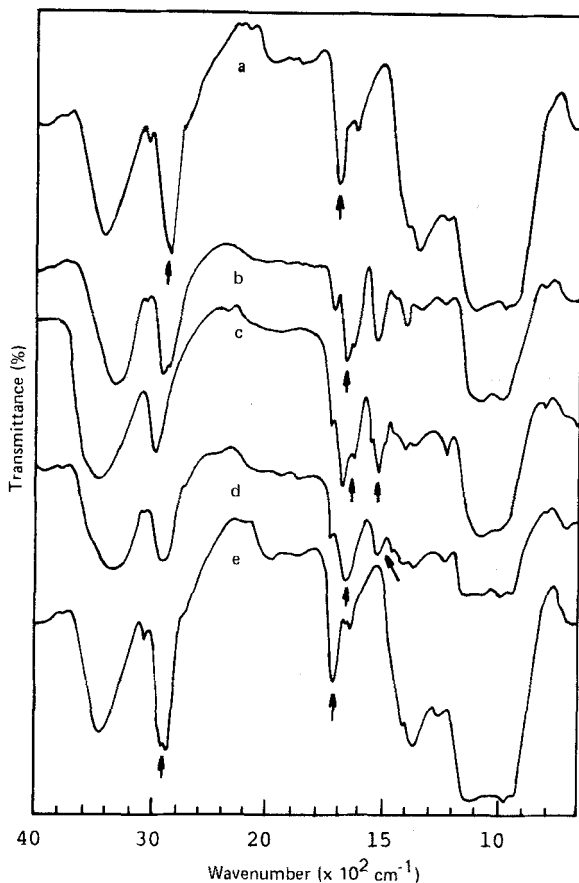


FIG. 3. IR spectra of poly-AL (a), AL-AAM radical copolymer (b), AL-AAm anionic copolymer containing hydrogen transfer polymerization (c), poly-AL in the presence of PAm (d), and poly-AL in the presence of AcAm (e).

In order to investigate the relation between the PAm concentration and the absorbance of the amide II band, the absorption law was used. A linear relationship was obtained from plots of  $\log I/I_0$  vs PAm concentration (Fig. 4). An increase in the amount of additive PAm produces an increase of absorbance. These results coincide with the results of elementary analysis.

The intrinsic viscosity  $[\eta]$  of poly-AL was measured in methanol at  $30^\circ\text{C}$  with an Ostwald viscometer. The relationship between  $[\eta]$  and the



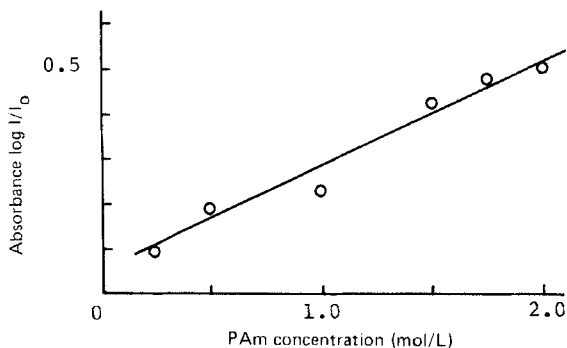


FIG. 4. The relation between PAm concentration and absorbance  $\log I/I_0$  depends on amide II of poly-AL.

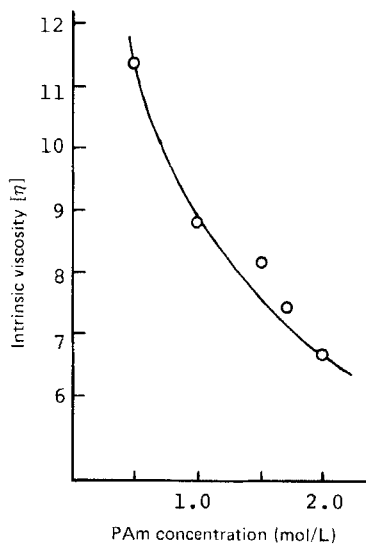
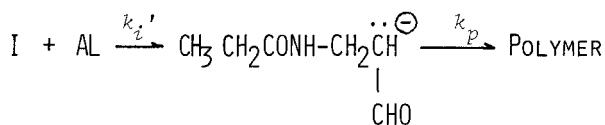
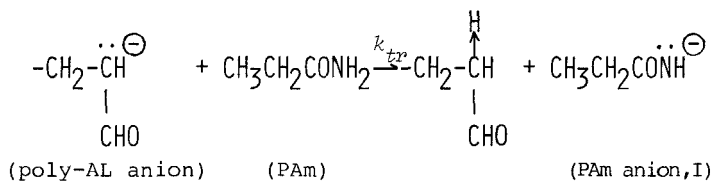


FIG. 5. The relationship between PAm concentration and the intrinsic viscosity of poly-AL.

PAm concentration is shown in Fig. 5. An increase of PAm concentration produces a decrease of  $[\eta]$ . These results clearly indicate the presence of a chain transfer reaction between the poly-AL anion and PAm.

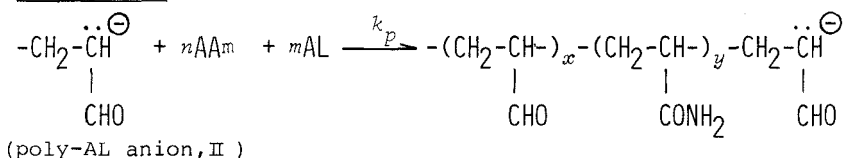
Hydrogen Transfer Polymerization Mechanism

In this work the existence of a chain transfer reaction became clear; that is, the polymerization of AL may be reinitiated by the PAm anion formed by the hydrogen transfer reaction between poly-AL anion and PAm:

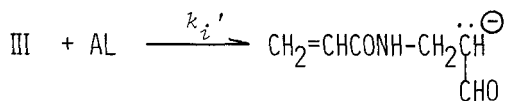
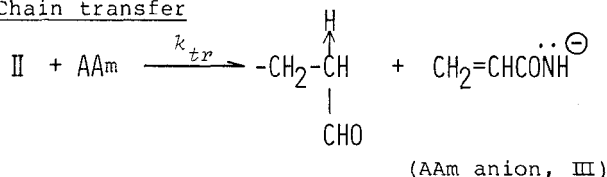


The hydrogen transfer polymerization mechanism of AAm with poly-AL anion can therefore be expressed as follows.

Propagation



Chain transfer



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Accepted by editor July 18, 1983

Received for publication August 15, 1983