

A New Photopolymerization System for Vinyl Monomers

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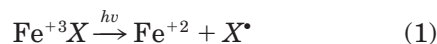
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ABSTRACT: A mixture of Ce^{+3} salt and an aminomethylene phosphonic acid, such as amino tri(methylene phosphonic acid) (ATMP), diethylene triamine penta(methylene phosphonic acid), *N,N*-di(methylene phosphonic acid) ethanol amine, *N,N*-di(methylene phosphonic acid)-*N*-methylamine, *N*-oxo-*N,N,N*-tri(methylene phosphonic acid), or 1-hydroxy-ethylidene-1,1-diphosphonic acid, was used for the photopolymerization of acrylonitrile, vinyl acetate, acrylic acid, and styrene in water. Molecular weights of the polymers decreased with increasing concentration of both Ce^{+3} salt and ATMP. The effect of oxygen, light, pH, and the addition order on polymerization were also studied. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2494–2499, 2002

Key words: cerious salt; aminomethylene phosphonic acid; photopolymerization; vinyl monomers; organophosphorous compounds

INTRODUCTION

Photopolymerization by metal or metal salts was reported on earlier^{1,2}:



Metal cations were said to be reduced with the anions by the effect of light, and the anions became radical or radical cation initiators. Photopolymerization of vinyl monomers with Ce^{+3} salts was also reported on before.^{3–5} Hydrogen radicals were suggested to be formed with a redox reaction by the effect of light in an acidic water solution and initiated polymerization.

Vinyl monomers were polymerized with the redox system of aminomethylenephosphonic acid

and ceric salts.⁶ Ce^{+4} was reduced to Ce^{+3} , and radicals were formed on aminomethylene phosphonic acid molecules that initiated polymerization of the vinyl monomers.⁶ During this work, sunlight caused some polymer formation from the mixture of acrylonitrile, aminomethylenephosphonic acid, and Ce^{+3} salt. Thus, the photopolymerization of vinyl monomers, with the mixture of Ce^{+3} salt and aminomethylenephosphonic acid was studied in this work.

EXPERIMENTAL

Materials

Ce^{+3} salt solution was prepared by dissolution of a calculated amount of cerium(III) nitrate (Fluka, Buchs, Switzerland) in water. Amino tri(methylene phosphonic acid) (ATMP), 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP), diethylene triamine penta(methylene phosphonic acid) (DT-PMPA), *N,N*-di(methylene phosphonic acid)-ethanol amine (DMPEA), and *N*-oxo-*N,N,N*-tri(methylene phosphonic acid) (OTMPA) were supplied by Monsanto (Brussels, Belgium). Polymerization grade monomers, including as acrylonitrile,

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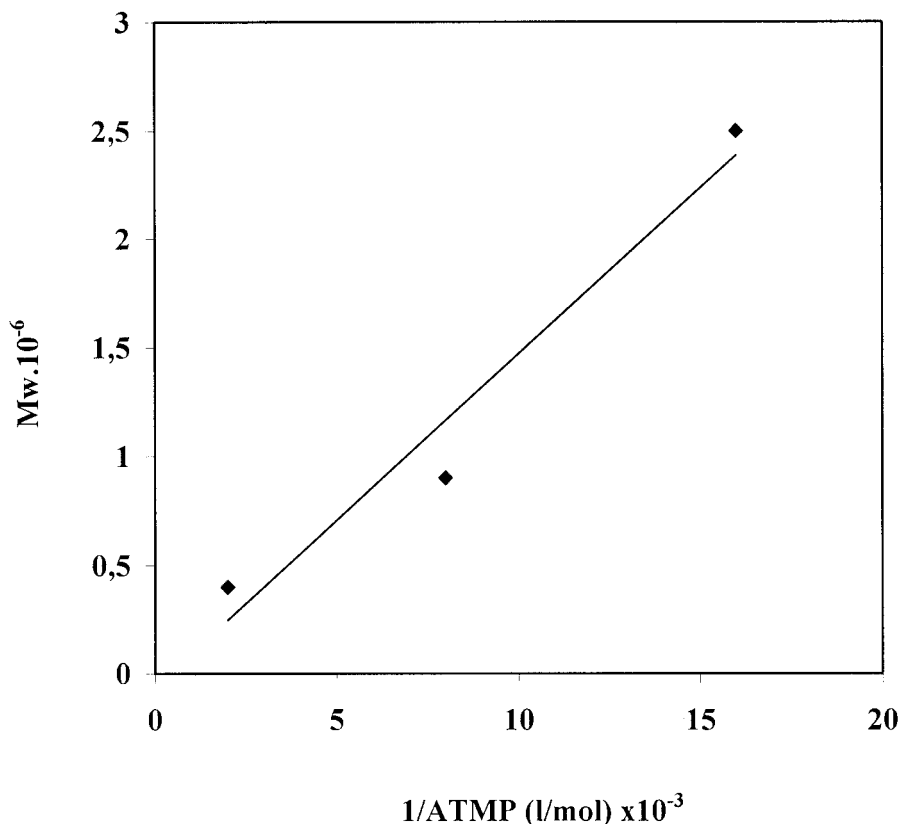


Figure 1 Effect of ATMP concentration on the molecular weight of polyacrylic acid. [Acrylic acid] = 0.73 mol/L; [Ce⁺³] = 20 mol/L; t = 4 h; T = 25°C.

acrylic acid, vinyl acetate, and 2-acrylamido-2-methylpropane sulfonic acid (AMPS), were used as received. We freed styrene from inhibitors by shaking with 10% NaOH solution.

Polymerization Procedure

Aminomethylenephosphonic acid was dissolved in water, and monomer was added. We degassed the contents of the flask by flushing with oxygen-free nitrogen. Cerium(III) nitrate stock solution was added to the reaction mixture under nitrogen atmosphere. The polymerization was allowed to proceed with stirring under the effect of sunlight for 4 h at room temperature. The polymers were recovered as follows:

1. Water-insoluble polymers precipitated during the polymerization. Some water was added into the reaction flask to allow flocculation of the precipitate. The powdery polymers were then filtered, washed several times with water and methanol, and finally dried under vacuum. They were purified by

reprecipitation in water from their dimethylformamide (DMF) solution. Polystyrene was formed both as emulsion and precipitate. The solution was filtered, and the emulsion was evaporated to dryness; then, polystyrene was extracted with CH₂Cl₂. Polystyrene purified by dissolution in 2-butanone and precipitation into methanol.

2. We precipitated out water-soluble polymers by pouring their viscous aqueous solutions into excess acetone. They were then filtered, washed with acetone, and finally dried under vacuum. In the case of poly(acrylic acid), the pH of polymerization solution was brought to about 10 with sodium hydroxyde solution, and then, the solution was poured into methanol. Precipitated polyacrylates were filtered, washed with methanol, and dried under vacuum.

In the absence of aminomethylenephosphonic acids, no polymer was formed in 4 h at room temperature in the light, when a similar experiment was carried out under comparable condi-

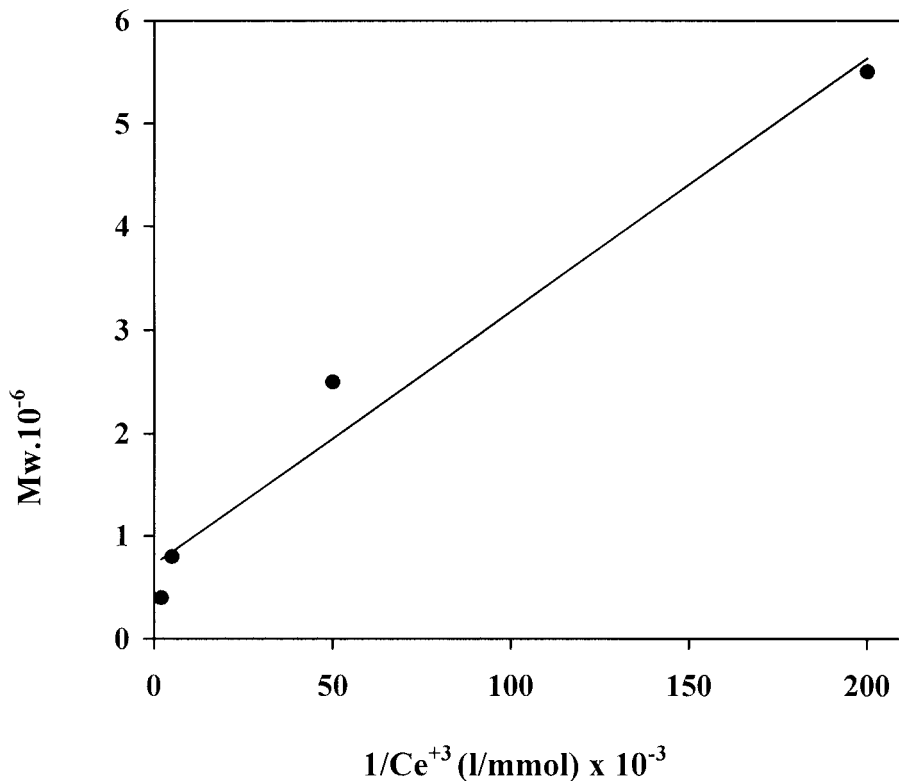


Figure 2 Effect of Ce^{+3} salt concentration on the molecular weight of polyacrylic acid. [Acrylic acid] = 0.73 mol/L; [ATMP] = 62 mmol/L; $t = 4$ h; $T = 25^\circ\text{C}$.

tions with a mixture of monomer and Ce^{+3} salt or a mixture of monomer and ATMP.

Molecular Weight

The viscosities of polyacrylonitrile solution in DMF at 25°C and polystyrene solutions in toluene at 30°C were measured with a Cannon-Fenske capillary viscometer (Analis, Namur, Belgium), and their molecular weights were calculated from single-point values. The following equations were used⁷⁻⁹:

$$[\eta] = \frac{\eta_{sp/c}}{1 + 0.28 \times \eta_{sp}}$$

$$[\eta] = 2.33 \times 10^{-4} M_w^{0.75} \quad (\text{for polyacrylonitrile})$$

$$[\eta] = 1.1 \times 10^{-4} M_n^{0.725} \quad (\text{for polystyrene})$$

where M_w is the weight-average molecular weight and M_n is the number-average molecular weight.

Poly(acrylic acid) was dissolved in 1.5N NaBr, and the viscosity was measured at 15°C ; molecu-

lar weights were calculated with following equation¹⁰:

$$[\eta] = 12.4 \times 10^{-4} \times M_w^{0.5}$$

RESULTS AND DISCUSSION

Both Ce^{+3} salt and aminomethylenephosphonic acid need to be present in the polymerization media to initiate the photopolymerization of vinyl monomers. Either of them alone did not photoinitiate the polymerization of vinyl monomers by the effect of sunlight.

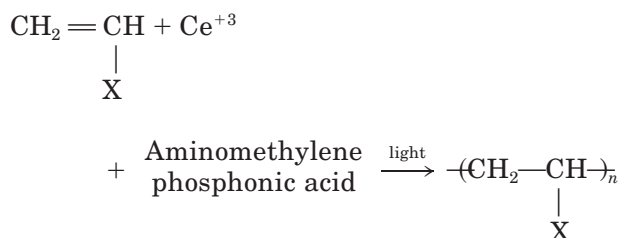


Table I Effect of the Concentrations of Ce^{+3} Salt and ATMP on the Photopolymerization of Acrylic Acid

Number	[ATMP] (mmol/L)	[Ce^{+3}] (mmol/L)	Yield (%)	M_n
1	62	5	94	5,500,000
2	62	20	90	2,500,000
3	62	200	88	800,000
4	62	500	82	380,000
5	124	20	90	900,000
6	496	20	70	410,000

[Acrylic acid] = 0.73 mol/L; t = 4 h; T = 25°C.

Effect of the Concentrations of Ce^{+3} Salt and Aminomethylenephosphonic Acid

The effects of the concentrations of Ce^{+3} salt and aminomethylenephosphonic acids on the yield and the molecular weight of polyacrylic acid are shown in Figures 1 and 2 and in Table I. The concentrations of both Ce^{+3} salt and ATMP had a significant effect on the molecular weight of the polymer rather than on the polymerization yield. An increase in the concentrations of both Ce^{+3} and ATMP resulted in decreasing trends of molecular weight, whereas the yields of polymerization were at level of similar values. The polymerization yield of 94% could be obtained even if Ce^{+3} salt concentration was as low as 5.0×10^{-3} mol/L. The polymerization was not terminated by any degradative chain-transfer reactions unless a very high concentration of ATMP (496 mmol/L) was used (Table I).

Effect of Aminomethylene Phosphonic Acid

A number of different aminomethylenephosphonic acids were used for photopolymerization of vinyl monomers to produce water-insoluble (Table II) and water-soluble polymers (Table III). The mixture of ATMP and HEDP was also used for the photopolymerization of acrylic acid (Table IV). The aminomethylenephosphonic acid/ Ce^{+3} salt system was very effective for the photopolymerization of vinyl monomers such as acrylonitrile, acrylic acid, acrylamide, and styrene but not for vinyl acetate (Table III). Vinyl acetate could only be copolymerized with acrylonitrile with this system. On the other hand, HEDP, which is an organophosphorous compound containing no amino groups, was very effective for the photopolymerization of vinyl acetate and acrylonitrile but was ineffective for the photopolymerization of acrylic acid (Table IV).

Effect of Light, Oxygen, and pH

Photopolymerizations were carried out both behind and in front of window glass in a glass flask under the effect of sunlight or with ultraviolet (UV) light in a quartz photopolymerization reactor. Similar yields were obtained. This shows that UV and visible regions of sunlight were effective for photopolymerization. The polymerization was probably initiated by radicals formed by the effect of light because a radical scavenger such as hydroquinone was inhibited the photopolymerization. Deliberate addition of oxygen to the system retarded the polymerization of acrylonitrile for

Table II Polymerization of Vinyl Monomers with Ce^{+3} Salt and Aminomethylenephosphonic Acids

Number	Aminophosphonic Acid		Monomer		Polymer	
	Type	Concentration (mmol/L)	Type	Concentration (mol/L)	Yield (%)	M_n
7	ATMP	62	Acrylonitrile	0.70	65	1,250,000
8	DTPMPA	64	Acrylonitrile	0.70	63	464,500
9	2086	—	Acrylonitrile	0.70	30	397,190
10	DMPEA	70	Acrylonitrile	0.70	35	891,250
11	OTMPA	60	Acrylonitrile	0.70	19	645,650
12	HEDP	100	Acrylonitrile	0.70	66	498,884
13	ATMP	70	Acrylonitrile/vinyl acetate	0.70/0.082	26	—
14	DTPMPA	60	Acrylonitrile/vinyl acetate	1.1/0.14	61	—
15	ATMP	60	Styrene	0.18	92	912,000

[Ce^{+3}] = 5×10^{-3} mol/L; t = 4 h; T = 25°C.

Table III Water-Soluble Vinyl Polymers Obtained with Photopolymerization in the Presence of Ce⁺³ Salt–Aminophosphonic Acid Compounds

Aminophosphonic Acid		Monomer		
Type	Concentration (mmol/L)	Type	Concentration (mol/L)	Polymer Yield (%)
ATMP	62	Acrylamide	0.40	100
H ₃ PO ₃	390	Acrylic acid	0.66	0
HEDP/ATMP	100/60	Acrylic acid/AMPS	0.66/0.02	100
ATMP	62	Acrylic acid/AMPS	0.66/0.02	100
HEDP/ATMP	100/60	Acrylic acid/AMPS	0.47/0.07	42
ATMP	62	Acrylic acid/AMPS	0.47/0.07	100
ATMP	62	Vinyl acetate	0.68	0

[Ce⁺³] = 5 mmol/L; *t* = 4 h; *T* = 25°C.

about 30 min, showing that oxygen was a retardant for this system.

The pH of the polymerization media was changed from 2 to 7 by the addition of NaOH solution before photopolymerization. No significant changes in the yield were observed.

Effect of Addition Order

Ce⁺³ salt solution was added to the mixture of ATMP and monomer, and photopolymerization began. If this order of addition was changed, there were no significant changes in the yield of the photopolymerization. In one experiment, Ce⁺³ salt was added to ATMP solution, and the precipitated complex was separated by filtration in the dark; when this ATMP–Ce⁺³ complex was added to a water solution of monomer, the light did not initiate photopolymerization. However, addition

of excess ATMP to this solution caused the photopolymerization to start.

CONCLUSIONS

The mixture of Ce⁺³ salt and aminomethylene-phosphonic acids was a very effective catalyst system for the photopolymerization of vinyl monomers in water. Radicals that were produced by a Ce⁺³ salt–ATMP complex under the effect of light initiated polymerization. The presence of a small amount of Ce⁺³ ions in the system was enough to initiate photopolymerization. Both water-soluble and water-insoluble monomers could be polymerized with this system. The molecular weight of the polymer was regulated by either cerium(III) salt or aminotrimethylenephosphonic acid concentrations. This system has many advantage over other initiation systems because the solvent is water, the polymerization is carried out at room temperature, a very small amount of cerium(III) salt is effective, and both visible light and UV light can be used. This system may also be used for the preparation of industrially important high-molecular-weight water-soluble polymers such as polyacrylic acid and polyacrylamide.

Table IV Effect of Organophosphorous Compounds on the Photopolymerization of Acrylic Acid

Aminophosphonic Acid	Concentration (mol/L)	Yield (%)	<i>M_n</i>
ATMP/HEDP	0.031/0.05	47	416,000
ATMP/HEDP	0.062/0.1	30	110,000 ^a
ATMP/HEDP	0.062/0.2	100	457,000
ATMP/HEDP	0.062/0.4	100	229,000
ATMP/HEDP	0.06/0	65	—
ATMP/HEDP	0/0.062	0	—

[Acrylic acid] = 0.66 mol/L; [Ce⁺³] = 20 mmol/L; *t* = 4 h; *T* = 25°C.

^a *T* = 40°C.

REFERENCES

1. Evans, M. G.; Santappa, M.; Uri, N. *J Polym Sci* 1950, 7, 243.
2. Mahedavan, V.; Santappa, M. *J Polym Sci* 1961, 1, 361.

3. Edgcombe, F. H. C.; Norrish, R. G. W. *Nature* 1963, 197, 282.
4. Hussain, F.; Norrish, R. G. W. *Proc R Soc A (London)* 1963, 275, 161.
5. (a) Scherwin, A. K. (to General Aniline & Film Corp.). Belg. Pat. 638, 336 (1964); (b) Scherwin, A. K. (to General Aniline & Film Corp.). U.S. Pat. Appl. (1962); Chem Abstr 1965, 62, 7290.
6. Öz, N.; Akar, A. *Eur Polym J* 2000, 36, 193.
7. Braun, D.; Cherdon, H.; Kern, W. *Practical Macromolecular Organic Chemistry*; Harwood: London, 1980; p 80.
8. Clelan, R. J.; Stockmayer, W. H. *J Polym Sci* 1955, 17, 473.
9. Danusso, F.; Moragho, G. *J Polym Sci* 1957, 24, 161.
10. Takahashi, A.; Nagasawa, M. *J Am Chem Soc* 1964, 86, 543.