

# Aqueous Polymerization of Methyl Methacrylate Initiated by Redox Pair: Ce(IV)–Azo Compounds with Methylol Functional Groups and Synthesis of Copolymers

U. TUNCA

Istanbul Technical University, Chemistry Department, Maslak, Istanbul 80626, Turkey

## SYNOPSIS

Hydroxyl functional azo compounds have been used as reducing agents in redox polymerization of methyl methacrylate (MMA) in conjunction with ceric ammonium nitrate (which acts as an oxidizing agent in aqueous nitric acid at 20°C). Kinetic measurements were followed by gravimetric method, at lower conversions, not exceeding 10% conversion. The dependence of rate of polymerization and average molecular weight, which was determined by gel permeation chromatography (GPC), on azo, Ce(IV), and MMA concentrations, respectively, were investigated. The homopolymers, which contain thermo- and photolabile azo groups, were utilized with different comonomers to give block or graft copolymers depending on termination mechanism of homopolymerization. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

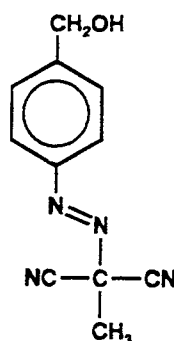
Ceric salts [Ce(IV)] have been used as initiators either with reducing agents, which were alcohols, thiols, aldehydes, and carboxylic acids, or alone in vinyl polymerization.<sup>1–4</sup>

When Ce(IV) salts are used in conjunction with suitable reducing agents, a free radical is produced in the reductant by an electron transfer.<sup>5–10</sup>

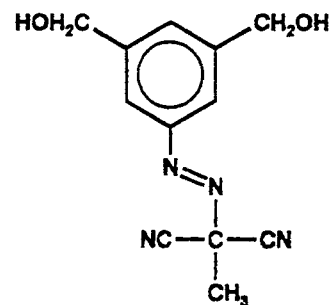
In our previous study,<sup>11</sup> some azo compounds, which have methylol functional groups, were used as reducing agents in the presence of Ce(IV) in order to initiate the polymerization of acrylamide in aqueous nitric acid solution at 20°C.

Redox reaction of Ce(IV) with HOCH<sub>2</sub> group containing thermo- or photosensitive azo compounds of type Azo I or Azo II prompted us to synthesize polymeric initiator with azo functions as head and tail group.<sup>11</sup> The number of azo groups per chain is controlled by termination mechanism. We now report a free radical polymerization of methyl methacrylate (MMA) initiated by a redox pair: Ce(IV)–Azo I with hydroxyl functional groups. The dependence of initial rate of polymerization on Azo I, Ce(IV), and MMA concentrations has been de-

termined in aqueous nitric acid solution at 20°C. Moreover, homopoly MMA, obtained from either redox pair Ce(IV)–Azo I or –Azo II containing thermo- or photolabile azo groups, was used as an initiator to form block or graft copolymer.



Azo I



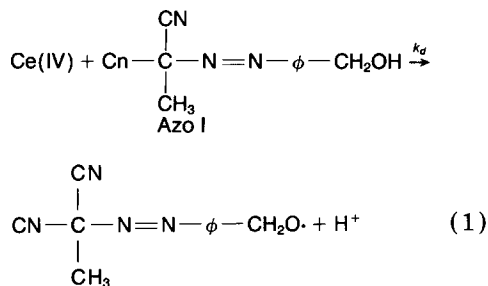
Azo II

## RESULTS AND DISCUSSION

### Reaction Mechanisms and Rate Law

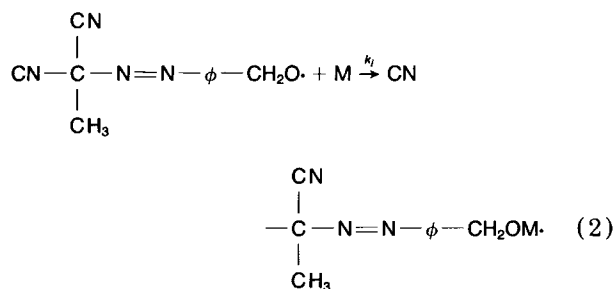
From the literature<sup>7–10</sup> and our present results, the following reaction mechanism is suggested:

Primary radical formation on azo compound:



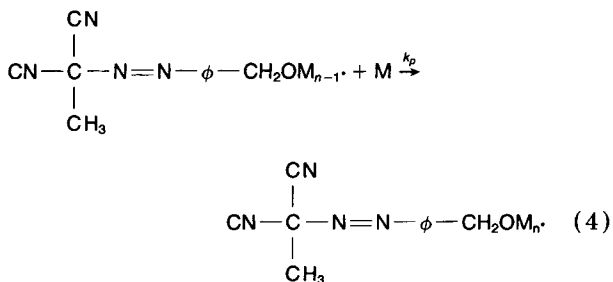
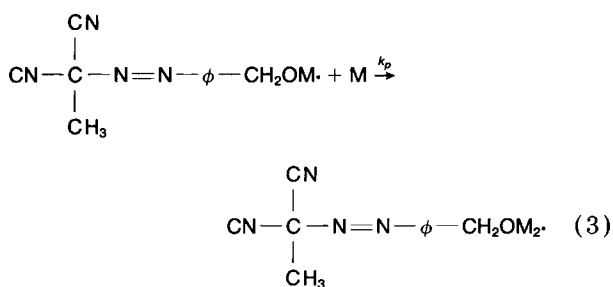
where  $\phi$  represents the *p*-phenylene group.

Initiation:

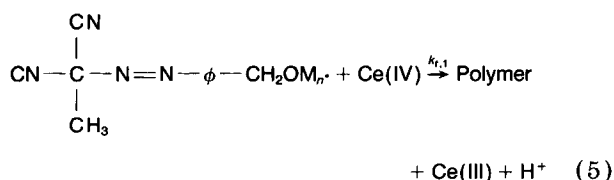


where M represents MMA.

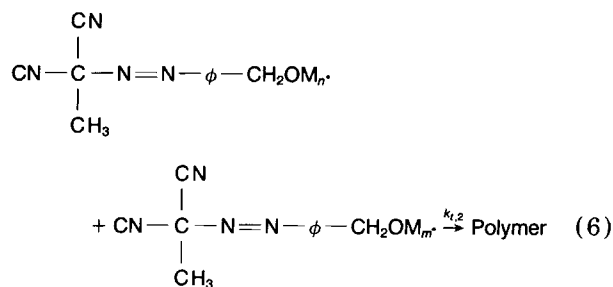
Propagation:



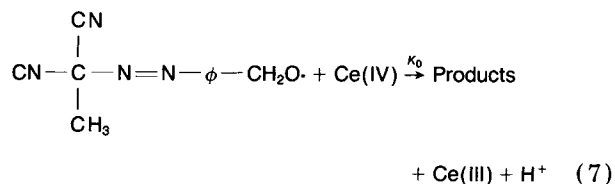
Linear termination (oxidative termination):



Bimolecular termination:



Oxidative termination of primary radicals:



By applying a steady-state principle to active intermediates, the following equation for  $R_p$  was derived for bimolecular termination:

$$R_p = \frac{k_p}{k_{t,2}^{1/2}} \left( \frac{k_i k_d [\text{Azo I}] [\text{Ce(IV)}]}{k_i [\text{M}] + k_0 [\text{Ce(IV)}]} \right)^{1/2} [\text{M}]^{3/2} \quad (8)$$

At lower concentrations of Ce(IV) ( $< 6 \times 10^{-4} M$ ), it can be assumed that  $k_0 [\text{Ce(IV)}] < k_i [\text{M}]$  and the above equation reduces to

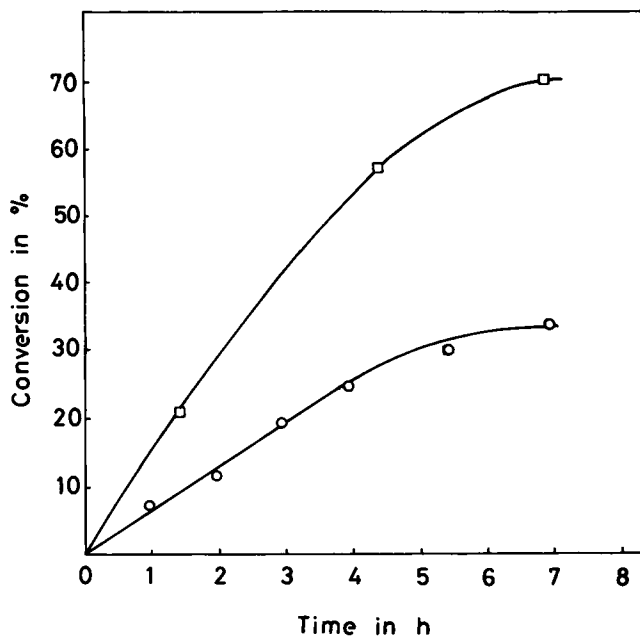
$$R_p = k_p \left( \frac{k_d}{k_{t,2}} \right)^{1/2} [\text{Azo I}]^{1/2} [\text{Ce(IV)}]^{1/2} [\text{M}] \quad (9)$$

### Relation between Conversion and Time

Maximum conversion is attained within 7 h (Fig. 1). The higher the Azo I and Ce(IV) concentrations the higher the time at which conversion attains maximum value.

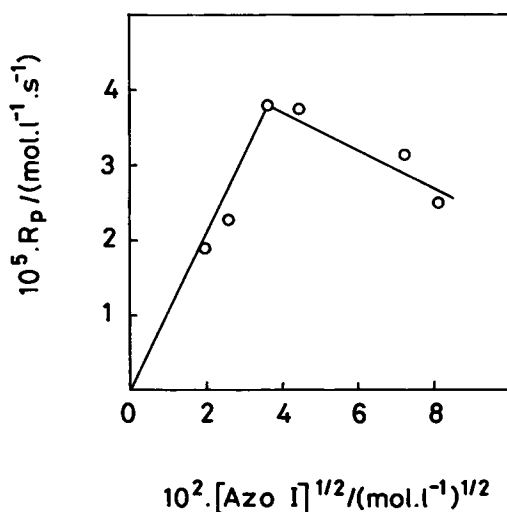
### Rate of Polymerization Dependence on Azo I Concentration

The concentration of Azo I was varied from  $3.9 \times 10^{-3} M$  to  $6.5 \times 10^{-3} M$  in order to evaluate its effect on the polymerization, keeping both  $[\text{MMA}] = 0.13 M$  and  $[\text{Ce(IV)}] = 5.6 \times 10^{-4} M$  constant. The rate of polymerization,  $R_p$ , increased with increasing Azo I concentration up to  $1.3 \times 10^{-3} M$ , being directly proportional to the square root of that concentration, clarifying the bimolecular termina-



**Figure 1** Plot of conversion vs. time: (O)  $[\text{Azo I}] = 3.25 \times 10^{-3} M$ ,  $[\text{Ce(IV)}] = 2.8 \times 10^{-3} M$ ; ( $\square$ )  $[\text{Azo I}] = 6.5 \times 10^{-3} M$ ,  $[\text{Ce(IV)}] = 5.6 \times 10^{-3} M$ ,  $[\text{MMA}] = 0.13 M$ ,  $[\text{HNO}_3] = 0.07 M$  at  $20^\circ\text{C}$ .

tion (Fig. 2). Beyond this point  $R_p$  decreased with increasing Azo I concentrations. Increasing the Azo I concentration enhanced the primary radical concentration, which caused an initial increase in  $R_p$ . Afterward, despite an increase in Azo I concentration,  $R_p$  decreased, which was due to a pretermination of active chains, as well as a termination of primary radicals<sup>7,8,11</sup> with Ce(IV), which was faster than the rate of initiation.



**Figure 2** Plot of  $R_p$  vs.  $[\text{Azo I}]^{1/2}$ :  $[\text{Ce(IV)}] = 5.6 \times 10^{-4} M$ ,  $[\text{MMA}] = 0.13 M$ ,  $[\text{HNO}_3] = 0.07 M$  at  $20^\circ\text{C}$ .

### Dependence on Concentration of Ce(IV)

Ce(IV) concentration was changed in the range of  $5.6 \times 10^{-5}$  to  $7.3 \times 10^{-4} M$ , with the remaining Azo I and MMA concentrations constant. The rate increased with increasing Ce(IV) concentration toward  $6 \times 10^{-4} M$ , being directly proportional to a half order of Ce(IV) concentration at  $20^\circ\text{C}$  (Fig. 3). Initial linear dependence of  $R_p$  on Ce(IV) reveals bimolecular termination. The decrease in  $R_p$  at higher Ce(IV) concentrations can be attributed to termination of active chains by Ce(IV).<sup>10</sup>

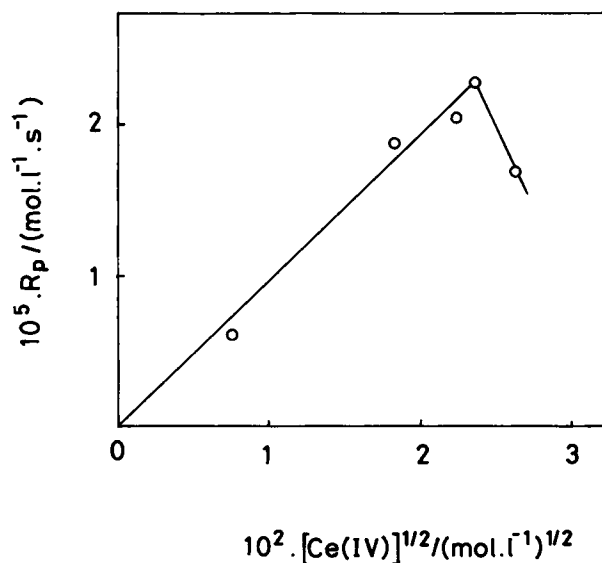
### Dependence on MMA Concentration

Keeping the other parameters constant, dependence of  $R_p$  on MMA concentration was investigated by increasing MMA concentration from 0.086 to 0.173 M. A regular increase in  $R_p$  was observed as MMA concentration increased, the order being unity (Fig. 4). This unity dependence indicates that bimolecular termination takes place predominantly.

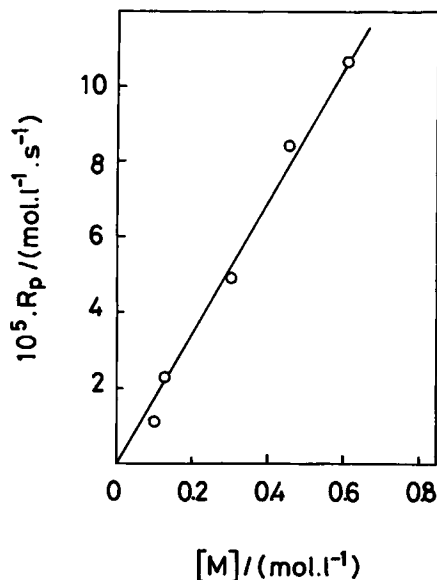
### Molecular Weight Dependence of Poly MMA

The average molecular weight of poly MMA, which was in the range of  $1.4\text{--}2.8 \times 10^4$  of  $M_n$  and  $7.0\text{--}10.9 \times 10^4$  of  $M_w$ , was almost independent with respect to conversion.

At lower Ce(IV) concentrations ( $< 6 \times 10^{-4} M$ ), assuming  $k_0 [\text{Ce(IV)}] < k_t [\text{M}]$ , the following equation can be derived:



**Figure 3** Plot of  $R_p$  vs.  $[\text{Ce(IV)}]^{1/2}$ :  $[\text{Azo I}] = 6.5 \times 10^{-4} M$ ,  $[\text{MMA}] = 0.13 M$ ,  $[\text{HNO}_3] = 0.07 M$  at  $20^\circ\text{C}$ .



**Figure 4** Plot of  $R_p$  vs.  $[MMA]$ :  $[Azo I] = 6.5 \times 10^{-4} M$ ,  $[Ce(IV)] = 5.6 \times 10^{-4} M$ ,  $[HNO_3] = 0.07 M$  at  $20^\circ C$ .

$$\overline{DP} = \frac{R_p}{R_t} = \frac{k_p[M]}{k_{t,2}^{1/2} k_d^{1/2} [Azo I]^{1/2} [Ce(IV)]^{1/2}} \quad (10)$$

where  $\overline{DP}$  represents the degree of polymerization. As can be seen from Eq. (10),  $\overline{DP}$  is directly proportional to  $M$  concentration and the inverse of the square root concentrations of Azo I and Ce(IV) (Figs. 5 and 6).

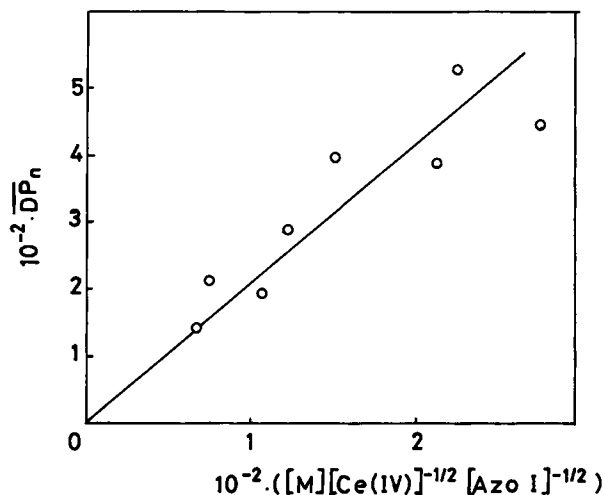
#### Azo Content of Homopoly MMA

Homopoly MMA, which was obtained from Azo I, has two azo end groups per chain in lower Ce(IV) concentrations ( $< 6 \times 10^{-4} M$ ) according to kinetic evidence. Moreover, an evaluation of differential scanning calorimetry (DSC) thermograms<sup>14</sup> of homopoly MMA almost supports this idea within the Ce(IV) concentration range indicated above. However, in higher Ce(IV) concentrations, oxidative termination becomes favorable and homopoly MMA includes one azo end group per chain.<sup>11</sup>

Redox reaction of Ce(IV) with Azo II enabled us to synthesize polymeric initiator (homopoly MMA) with azo functions as tail groups. DSC traces of homopoly MMA obtained from the above redox pair showed about one pendant azo group per chain.

#### Block and Graft Copolymer Synthesis

Block and graft copolymers were synthesized by employing homopoly MMA as initiator owing to its labile terminal or pendant azo group corresponding



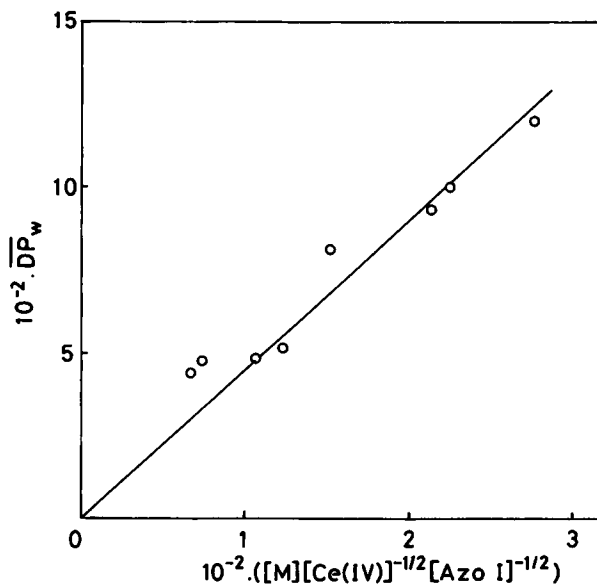
**Figure 5** Plot of  $DP_n$  vs.  $[M][Ce(IV)]^{-1/2}[Azo I]^{-1/2}$ , at  $20^\circ C$ .

with Azo I and II, respectively. Acrylamide (AAM) and styrene (St) were used as comonomers to synthesize block or graft copolymers. The cumulative results were tabulated in Tables I-IV.

#### THERMAL CHARACTERIZATION OF BLOCK AND GRAFT COPOLYMERS

Thermal analysis of block and graft copolymers was carried out using DSC to obtain their glass transition temperatures ( $T_g$ ) (Table V).

Multiplicity of  $T_g$  in block or graft copolymers,



**Figure 6** Plot of  $DP_w$  vs.  $[M][Ce(IV)]^{-1/2}[Azo I]^{-1/2}$ , at  $20^\circ C$ .

**Table I Block Copolymerization<sup>a</sup> of Poly MMA, Obtained from Azo I–Ce(IV) Redox Pair, with AAm**

Poly MMA <sup>b</sup>			AAm		Composition of the Reaction Mixture			Block Copolymer Composition <sup>c</sup>
Conc. (g × L <sup>-1</sup> )	Mol. (M <sub>w</sub> × 10 <sup>-4</sup> )	Mass <sup>c</sup> (M <sub>n</sub> × 10 <sup>-4</sup> )	Conc. (mol × L <sup>-1</sup> )	Conversion <sup>d</sup> (%)	pMMA Block (wt %)	pAAm (wt %)		pAAm (mol %)
20	5.91	2.29	0.384	97	37	52	11	64

<sup>a</sup> Carried out in dioxan for 68 h at 70°C.<sup>b</sup> [Ce(IV)] = 5.6 × 10<sup>-3</sup>M, [Azo I] = 6.5 × 10<sup>-3</sup>M, [MMA] = 1.3M, [HNO<sub>3</sub>] = 0.07M, at 20°C.<sup>c</sup> Determined from RI detector of GPC; azo content per polymer chain calculated from DSC thermogram: 1.35.<sup>d</sup> Overall AAm conversion.<sup>e</sup> Calculated by FT-IR.**Table II Block Copolymerization<sup>a</sup> of Poly MMA, Obtained from Azo I–Ce(IV) Redox Pair, with St**

Poly MMA <sup>b</sup>			St		Composition of the Reaction Mixture			Block Copolymer Composition <sup>e</sup>	Mol. Mass of Block Copolymer	
Conc. (g × L <sup>-1</sup> )	Mol. (M <sub>w</sub> × 10 <sup>-4</sup> )	Mass <sup>c</sup> (M <sub>n</sub> × 10 <sup>-4</sup> )	Conc. (mol × L <sup>-1</sup> )	Conversion <sup>d</sup> (%)	pMMA Block (wt %)	pSt (wt %)		pSt (mol %)	M <sub>w</sub> × 10 <sup>-4</sup>	M <sub>n</sub> × 10 <sup>-4</sup>
16.9	7.3	1.4	2.65	10	36	49	15	85	88.1	42.1

<sup>a</sup> Carried out in benzene for 48 h at 70°C.<sup>b</sup> [Ce(IV)] = 2.8 × 10<sup>-3</sup>M, [Azo I] = 3.25 × 10<sup>-3</sup>M, [MMA] = 1.3M, [HNO<sub>3</sub>] = 0.07M at 20°C.<sup>c</sup> Determined from RI detector of GPC; azo content per polymer chain calculated from DSC thermogram: 1.61.<sup>d</sup> Overall St conversion.<sup>e</sup> Calculated by <sup>1</sup>H-NMR.**Table III Graft Copolymerization<sup>a</sup> of Poly MMA, Obtained from Azo II–Ce(IV) Redox Pair, with AAm**

Poly MMA <sup>b</sup>			AAm		Composition of the Reaction Mixture			Block Copolymer Composition <sup>e</sup>
Conc. (g × L <sup>-1</sup> )	Mol. (M <sub>w</sub> × 10 <sup>-4</sup> )	Mass <sup>c</sup> (M <sub>n</sub> × 10 <sup>-4</sup> )	Conc. (mol × L <sup>-1</sup> )	Conversion <sup>d</sup> (%)	pMMA Block (wt %)	pAAm (wt %)		pAAm (mol %)
6.9	8.6	1.2	1.46	13	26	44	30	71.4

<sup>a</sup> Carried out in dioxan for 68 h at 70°C.<sup>b</sup> [Ce(IV)] = 1.12 × 10<sup>-2</sup>M, [Azo II] = 5.7 × 10<sup>-3</sup>M, [MMA] = 1.3M, [HNO<sub>3</sub>] = 0.07M at 20°C.<sup>c</sup> Determined from RI detector of GPC; azo content per polymer chain calculated from DSC thermogram: 1.15.<sup>d</sup> Overall AAm conversion.<sup>e</sup> Calculated by FT-IR.

which contain AAm segment, was observed. It was reported that if each block was of reasonable size, the single links between blocks would have been insufficient to overcome their mutual incompatibilities.<sup>12</sup> Hence, two phases would be incompatible and

a thermogram would show two  $T_g$ 's, which would be close to  $T_g$ 's of corresponding homopolymers.<sup>12</sup> Block and graft copolymers of MMA–St have only one  $T_g$ , which is consistent with the values given in the literature.<sup>12</sup>

**Table IV Graft Copolymerization<sup>a</sup> of Poly MMA, Obtained from Azo II–Ce(IV) Redox Pair, with St**

Poly MMA <sup>b</sup>			St	Conversion <sup>d</sup> (%)	Composition of the Reaction Mixture			Graft Copolymer Composition <sup>e</sup>	Mol. Mass of Graft Copolymer	
Conc. (g × L <sup>-1</sup> )	Mol. (M <sub>w</sub> × 10 <sup>-4</sup> )	Mass <sup>c</sup> (M <sub>n</sub> × 10 <sup>-4</sup> )	Conc. (mol × L <sup>-1</sup> )		pMMA	pSt	Block (wt %)	pst (mol %)	M <sub>w</sub> × 10 <sup>-4</sup>	M <sub>n</sub> × 10 <sup>-4</sup>
14.7	6.1	0.85	2.62	13	12	58	30	83	68.2	36.1

<sup>a</sup> Carried out in benzene for 96 h at 70°C.

<sup>b</sup> [Ce(IV)] = 1.68 × 10<sup>-2</sup>M, [Azo II] = 5.7 × 10<sup>-3</sup>M, [MMA] = 0.13M, [HNO<sub>3</sub>] = 0.07M at 20°C.

<sup>c</sup> Determined from RI detector of GPC; azo content per polymer chain calculated from DSC thermogram: 1.20.

<sup>d</sup> Overall St conversion.

<sup>e</sup> Calculated by <sup>1</sup>H-NMR.

## EXPERIMENTAL

### General Remarks

<sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded with a Bruker AC 250 (250 MHz for protons, 62.9 MHz for carbons). Infrared (IR) spectra were measured with a Digilab FTS-40 FTIR spectrophotometer. Gel permeation chromatography (GPC) curves were monitored with a Waters ALC 200 [THF as eluent, RI and ultraviolet (UV) detection (254 nm), polystyrene, and poly MMA standards]. DSC thermograms were taken by a Perkin-Elmer DSC-7, which had been calibrated with indium.

### Compounds and Syntheses

Methyl methacrylate (MMA) (Merck), styrene (St) (Merck), and acrylamide (AAM) (Merck) were purified by conventional methods and immediately used. Ceric ammonium nitrate [Ce(IV)] (Aldrich) was used as received. 4-(1,1-dicyanoethylazo) benzyl alcohol (Azo I) and 3,5-di(hydroxymethyl)phenyl azomethyl malonodinitrile (Azo II) were synthesized according to the literatures.<sup>13,14</sup>

Polymerization and copolymerization were carried out in Schlenk tubes, which have thermostated water jackets. Some details about redox polymerization were given in a previous study.<sup>11</sup> Kinetic measurements were followed gravimetrically and conversion data, less than 10%, were evaluated.

Poly MMA and poly St were removed from block or graft copolymers by extractive separation.<sup>15</sup> Poly MMA and poly AAM were separated from block or graft copolymers according to following method. The mixture was extracted with a boiling benzene and water, respectively.

## CONCLUSION

Since Azo I and II are water-soluble initiators, and chosen MMA concentrations fit solubility limits in water (2%), an aqueous polymerization of MMA, initiated by redox system, first occurs as a homogeneous polymerization. During the course of polymerization, when homopoly MMA are no longer soluble, the system becomes heterogeneous.<sup>7</sup> The kinetic evaluation was applied only for the initial step of polymerization.

**Table V Thermal Characterization of Copolymers**

Block or Graft Copolymers	$T_{g1}$	$T_{g2}$	$\Delta C_{p1}$	$\Delta C_{p2}$
	°C		J × g <sup>-1</sup> °C <sup>-1</sup>	
Poly (MMA- <i>b</i> -AAM) <sup>a</sup>	123.7	180.2	0.097	0.080
Poly (MMA- <i>b</i> -St) <sup>b</sup>	92.7		0.177	
Poly (MMA- <i>g</i> -AAM) <sup>b</sup>	124.7	192.0	0.073	0.255
Poly (MMA- <i>g</i> -St) <sup>b</sup>	94.2		0.061	

<sup>a</sup> Heating rate is 10°C min<sup>-1</sup>.

<sup>b</sup> Heating rate is 20°C min<sup>-1</sup>.

The kinetic measurements and DSC thermograms showed that the homopoly MMA, obtained from redox pair Ce(IV)–Azo I in aqueous nitric acid medium, contained two azo terminal group per chain in lower Ce(IV) concentrations ( $< 6 \times 10^{-4} M$ ). However, in higher Ce(IV) concentrations, linear termination mechanism becomes favorable, providing one terminal azo group per chain.

When a redox pair Ce(IV)–Azo I is used, by varying Ce(IV) concentration, one can adjust azo group concentration per homopolymer chain and eventually block copolymer type.

The author would like to thank the Alexander von Humboldt Foundation for a financial support.

## REFERENCES

1. G. Mino, S. Kaizermann, and E. Rasmussen, *J. Polym. Sci.*, **38**, 393 (1959).
2. H. Riaz, L. V. Marajan, and Q. Anwaruddin, *Makromol. Chem.*, **179**, 1193 (1978).
3. S. K. Saha and A. K. Choudhary, *J. Polym. Sci., Part A-1*, **10**, 797 (1958).
4. J. Saldick, *J. Polym. Sci.*, **19**, 73 (1956).
5. U. Tunca, I. E. Serhatli, and Y. Yagci, *Polym. Bull. (Berlin)*, **22**, 483 (1989).
6. G. S. Misra and U. D. N. Bajpai, *Prog. Polym. Sci.*, **8**, 61 (1982).
7. M. D. Fernandez and G. M. Guzman, *Eur. Polym. J.*, **26**, 301 (1990).
8. M. D. Fernandez and G. M. Guzman, *Brit. Polym. J.*, **21**, 413 (1989).
9. N. Mohanty, B. Paradhan, and M. C. Mohanta, *Eur. Polym. J.*, **15**, 743 (1979).
10. A. Rout, S. P. Rout, B. C. Singh, and M. Santappa, *Makromol. Chem.*, **178**, 639 (1979).
11. U. Tunca, *Eur. Polym. J.*, submitted.
12. S. W. Shalaby and H. E. Blair, Block Copolymers and Polyblends, in *Thermal Characterization of Polymeric Materials*, E. A. Turi, Ed., Academic Press, New York, 1981, pp. 394–395.
13. O. Nuyken and U. Presenz, *Polym. Bull. (Berlin)*, **20**, 335 (1988).
14. O. Nuyken and R. Weidner, *Adv. Polym. Sci.*, **73/74**, 147 (1986).
15. I. Piirma and L. P. H. Chou, *J. Appl. Polym. Sci.*, **24**, 2051 (1979).

Received February 21, 1994

Accepted May 19, 1994