Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Yamazaki, Noboru , Tanaka, Itsuro and Nakahama, Seiichi(1968) 'Electroinitiated Anionic Polymerization of Vinyl Monomers', Journal of Macromolecular Science, Part A, 2: 6, 1121 — 1137

To link to this Article: DOI: 10.1080/10601326808051883

URL: http://dx.doi.org/10.1080/10601326808051883

J. MACROMOL. SCI.—CHEM, A2(6), pp. 1121-1137, October, 1968

Electroinitiated Anionic Polymerization of Vinyl Monomers

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SUMMARY

Polarographic reduction and electrolytically initiated anionic polymerization of various monomers have been investigated with tetra-n-butylammonium perchlorate in dimethoxyethane.

In polarographic studies, half-wave potentials of 10 vinyl monomers were measured and these values were found to be linearly related with the Hammett's σ values. The direct addition of electrons to monomer from the cathode initiate polymerizations and has been successfully performed by controlling the cathode potential at which the monomer alone could be reduced. The electroinitiated polymerization of methacrylonitrile has been investigated in detail. The yield of the polymer depended on the amount of current, and the molecular weight of the polymer was found proportional to the concentration of the monomer.

INTRODUCTION

Recently the polymerization of vinyl monomers by means of electrolytic process has received much attention [1-3]. It has been reported from our laboratory that the electrolytic polymerization of α-methylstyrene with $NaAl(C_2H_5)_4$ as a supporting electrolyte produced "living polymer" in tetrahydrofuran [4]. In the same paper, we made some incorrect suggestions from the i-V curves measured in the presence and in the absence of the monomer in tetrahydrofuran containing $NaAl(C_2H_5)_4$ that the direct attack of electron on the double bond of the monomer might occur at cathode.

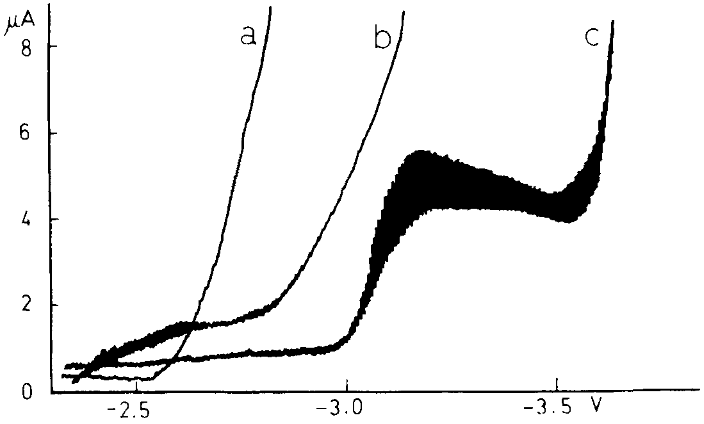
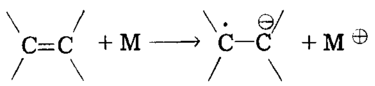


Fig. 1. Polarograms of Li^+ (a), Na^+ (b), and α-methylstyrene (c) at 25°C. Tetrabutylammonium perchlorate was used as a supporting electrolyte.

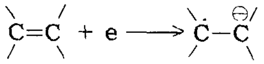
This incorrect suggestion arose, first, by ignoring the large amount of iR drop in the solution. Second, the deposit of the reduced products on the cathode surface might influence the observed voltage, since the solution was not stirred vigorously. In order to demonstrate the accurate mechanism of the reaction, polarographic studies were carried out and it was found that the reduction potentials of alkali metal cations were more negative than that of α-methylstyrene, as shown in Fig. 1. Thus it was concluded that indirect electron transfer through the alkali metal reduced at cathode initiated the polymerization when alkali metal salts were used as supporting electrolytes:

$$M^{\oplus} + e \longrightarrow M$$



$$\rangle C{=}C\langle \; + M \longrightarrow \rangle\dot{C}{-}\overset{\ominus}{C}\langle \; + M^{\oplus} \qquad \text{(M is alkali metal)} \qquad (1)$$

Although several reports of studies on electroinitiated anionic polymerization of styrene [5], α-methylstyrene [6], isoprene [7], methyl methacrylate [8], acrylonitrile [8], and 4-vinylpyridine [9] have been published, a clear indication of the mechanism of the initiation reaction has not been obtained. Funt and Williams [8] reported the electroinitiated polymerization of acrylonitrile in dimethylformamide using alkali metal salts such as $NaNO_3$ as a supporting electrolyte and suggested that the initiation proceeded via direct electron transfer to the double bond as shown in Eq. (2).



$$\mathrm{>C{=}C<} + e \longrightarrow \mathrm{>\dot{C}{-}\overset{\ominus}{C}<} \qquad (2)$$

In the polarographic measurement, the half-wave potentials of acrylonitrile, sodium cation, and lithium cation were observed to be −1.69, −1.55, and −1.95 V, respectively, vs. mercury pool. From these measurements it might be deduced that acrylonitrile was reduced via indirect electron transfer in accordance to Eq. (1), initiating the polymerization in dimethylformamide containing sodium salt.

Polymerization initiated by direct electron transfer, however, could be possible if electrolysis is conducted in the following conditions: (1) the reduction potential of the supporting electrolyte used is more negative than those of monomers, (2) the solution has high electric conductivity, and (3) an aprotic solvent such as ether is used to avoid the termination by proton. In this paper we wish to report the polarographic studies of various vinyl monomers in an aprotic solvent as dimethoxyethane containing tetra-n-butylammonium perchlorate, which has a more negative reduction potential than that of monomers, as well as the results of the direct electron transfer polymerization of these monomers at the controlled potentials based on the measurement of the half-wave potentials of the monomers.

EXPERIMENTAL

Materials

Dimethoxyethane, Ansul Co., was dried over $LiAlH_4$ and distilled.

Supporting electrolyte (Bu_4NClO_4) was synthesized from tetrabutylammonium iodide and silver perchlorate [10] and recrystallized from ethyl acetate.

All vinyl monomers were fractionally distilled and stored over CaH_2 and redistilled prior to use.

Measurement of Half-Wave Potential ($E_{1/2}$)

The measurements of half-wave potentials of vinyl monomers were performed at 25°C under nitrogen atmosphere using the apparatus shown in Fig. 2. The cell, which contained the supporting electrolyte, was dried under vacuum for about 5 hr and then the solvent, dimethoxyethane, was introduced via the trap-to-trap method. The concentrations of the supporting electrolyte and the monomers were 0.1 and 0.001 mole/liter respectively.

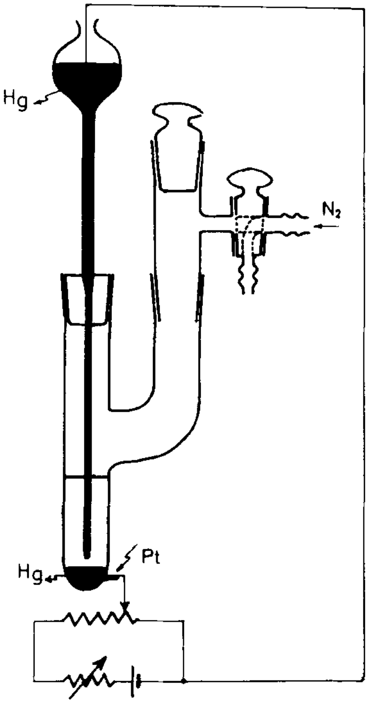


Fig. 2. Polarograph cell.

The potential at 25°C of the reference mercury pool electrode covered with the solution of 0.1 M Bu_4NClO_4 in dimethoxyethane, was −0.3 V vs. the aqueous saturated calomel electrode (SCE). The corrected values of potentials (Table 1) vs. SCE were obtained by adding −0.3 V to the observed potentials vs. the mercury pool.

Polymerization

Polymerization was carried out in the modified H-type glass cell which was separated into two compartments by sintered glass as shown in Fig. 3. The total volume of the cell was approximately 60 ml. The smooth platinum electrodes (C) and (D), each 3.5 × 1.0 cm^2 and 6 cm apart, were permanently sealed into the apparatus.

In order to achieve the polymerization by a direct electron transfer process, it is necessary to obtain the appropriate cathode potential for polymerization at which the monomer alone can be reduced and the electrolyte is not affected. In the thoroughly dried

Table 1. Half-Wave Potentials of Monomers

Monomer	$-E_{1/2}$ vs. SCE, V	$-E_{1/2}$ vs. SCE,[a] V	$L_{\bar{\beta}}$ [b]
Acrylonitrile	2.09	2.01	1.240
Methacrylonitrile	3.13		1.283
Methyl acrylate	2.95	1.95	1.428
Methyl methacrylate	3.07	2.01	1,511
Butadiene	3.27	2.60	1.644
Styrene	3.19	2.35	1.704
Chloroprene	2.95, 3.41		1.717
Isoprene	3.43	2.70	1.743
α-Methylstyrene	3.28	2.39	1.843
Vinyl acetate	No wave		2.130
Vinyl chloride	No wave		2.173
Vinylidene chloride	3.22		

[a] Measured in dioxane-water [13].
[b] Anionic β-carbon localization energy given in units of $-\beta$ [13].

dimethoxyethane solution, however, it was difficult to measure the absolute cathodic potential with the aqueous saturated calomel electrode or other reference electrodes. Instead of the absolute potential, the potential difference was measured between the cathodic electrode (C) and the auxiliary electrode of platinum wire (E) sealed into the glass tube and kept as close to the cathodic electrode as possible. The auxiliary electrode (E) seemed to have the same potential as that of the solution near the cathode and iR drop was negligible because of high internal resistance, 10 MΩ, of the voltmeter used. Thus the potential difference between (C) and (E) seemed to parallel the cathode potential, although the potential difference was a tentative measure and had no distinct physical implication.

Before and after distillation of the monomer into the cell, the value of the current was plotted vs. the cathode potential as shown in Fig. 6. From these i-V curves, the appropriate cathode potential for the electrolysis was determined.

After electrolysis, the catholyte was treated with methanol HCl and the volatile components were removed under reduced pressure. The low polymers were extracted in diethyl ether from the residue.

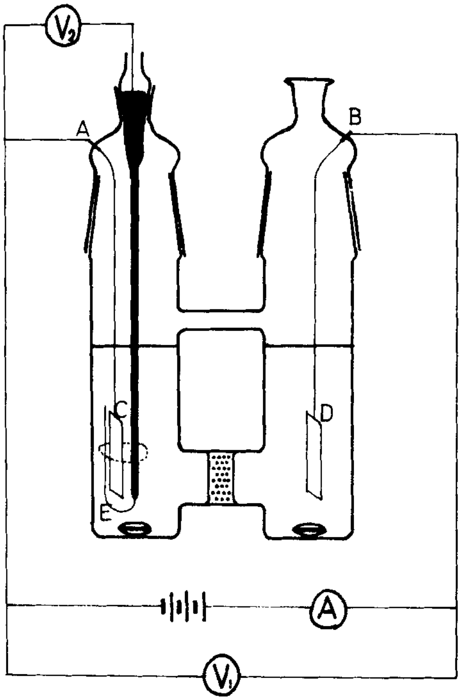


Fig. 3. Electrolysis cell. Ⓐ, ammeter; Ⓥ_1 and Ⓥ_2, voltmeter (PM-18c, Toa Dempa Co.,); A and B, permanent seal; D, anode; C, cathode; E, auxiliary electrode.

RESULTS AND DISCUSSION

Half-Wave Potentials of Several Monomers

The experimental results are shown in Table 1 and Fig. 4. The half-wave potentials were obtained with nine monomers of conjugated systems. On the other hand, no reduction wave was observed of monomers of unconjugated systems such as vinyl acetate and vinyl chloride, except vinylidene chloride, which had a reduction wave at −3.22 V vs. SCE. Although vinylidene chloride is not conjugated, it can be found in the vicinity of the region of the conjugated system in the Q-e map [11] and polymerized by anionic catalysts [12]. A small amount of low polymer of vinylidene chloride was actually obtained by electroinitiated polymerization.

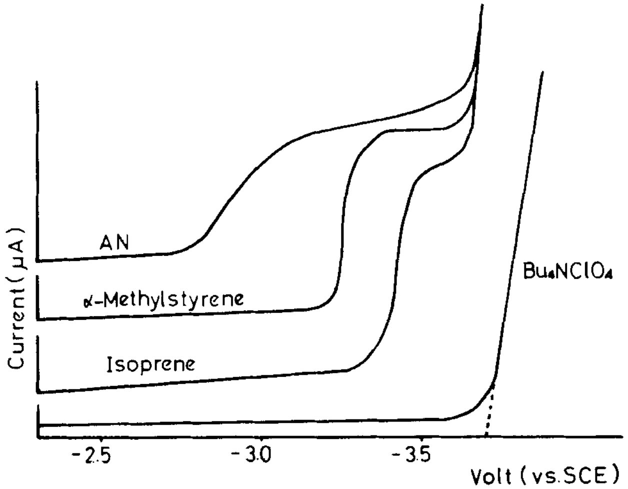


Fig. 4. Polarograms of several monomers. Monomer concentration, 10^{-3} mole/liter; h_{Hg}, 70 cm; temp., 25°C; supporting electrolyte, 0·1 M Bu_4NClO_4.

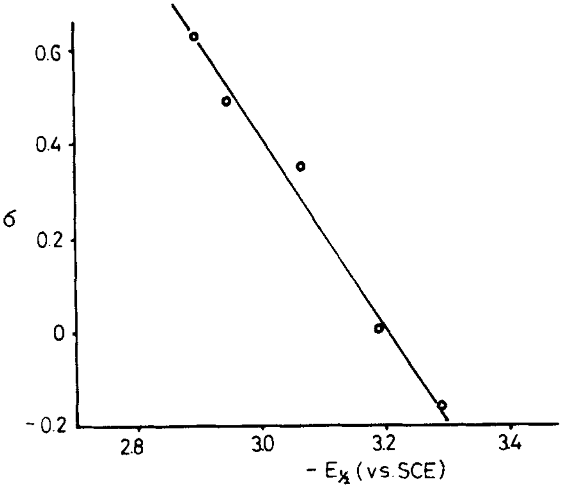


Fig. 5. Relationship between half-wave potentials of the monomers and Hammett's σ values.

The half-wave potentials of the monomers measured in dry dimethoxyethane were more negative than those measured in dioxane-water [13, 14] or in dimethylformamide [15, 16], although the potentials of these monomers were in the same order. As reported by Fueno et al. [13], the linear relationships were also found among the half-wave potentials of the monomers and the Hammett's σ values, as shown in Fig. 5, and L_{β}^{-}, which were the anionic β-carbon localization energies of the monomers listed in Table 1.

More positive potentials were observed with acrylonitrile, styrene, methyl acrylate, and butadiene compared with the corresponding methyl-substituted monomers: methacrylonitrile, α-methylstyrene, methyl methacrylate, and isoprene, respectively. This may be attributed to the I effect of the methyl group at the double bond.

From the general polarographic equation, n, the number of electron transferred in the polarographic reduction, was determined to be 0. 54 for α-methylstyrene, and this value indicated that the initiation step was irreversible for the monomer.

Polymerization

α-Methylstyrene and Styrene. The electrolysis of α-methylstyrene was conducted at the potential difference between the cathodic electrode (C) and the auxiliary electrode (E) (Fig. 3), which is shown by a dashed line in Fig. 6. At this potential difference,

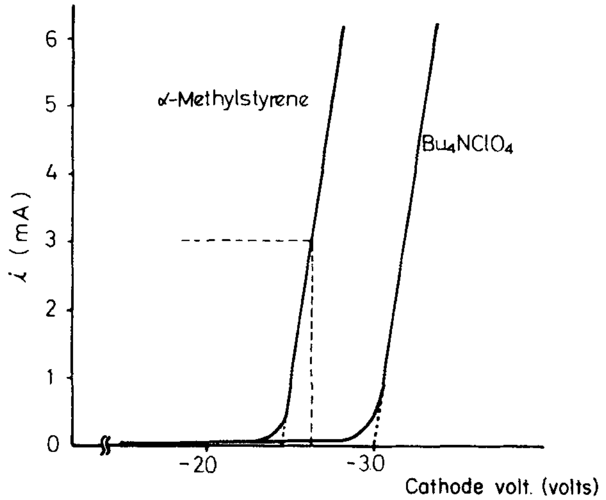


Fig. 6. i-V curves of α-methylstyrene and tetrabutylammonium perchlorate in dimethoxyethane.

almost all current might be consumed in the direct electron transfer to the double bond of α-methylstyrene from a platinum electrode. During the electrolysis of α-methylstyrene in dimethoxyethane, the red color of the carbanion was observed around the cathode, which got distributed and vanished quickly [6]. After electrolysis, only the low polymers of molecular weights in the range 300-500 were found in the cathodic compartment, but no trace of polymer was in the anolyte. Since tri-n-butylamine was detected in the catholyte by gas chromatography and identified by the formation of the salt of the amine with 2, 4-dihydroxybenzoic acid (m.p. 122°C, authentic m.p. 121°C [17]), it was understood that the carbanion at growing end reacted with the ammonium ion. In the termination step, two possible reactions are postulated; the polymer carbanion abstracts proton and butyl cation from the ammonium ion, as shown in Eqs. (3) and (4), respectively. Tri-n-butylamine is formed in both the cases:

$$\begin{tikzcd} & \sim CH + C_4H_8 + (C_4H_9)_3N \qquad (3) \\ \sim C^{\ominus} + (C_4H_9)_4N^{\oplus} \arrow[ur] \arrow[dr] & \\ & \sim C-C_4H_9 + (C_4H_9)_3N \qquad (4) \end{tikzcd}$$

From the following experiments, the proton abstraction [Eq. (3)], rather than the reaction with butyl cation [Eq. (4)], was confirmed to occur predominantly. A dimethoxyethane solution of living polymer of α-methylstyrene was made with sodium metal and separated into two parts. One was killed by tetra-n-butyl ammonium perchlorate (I) and the other by butyl iodide in order to obtain the polymer containing the butyl end group (II). The presence of butyl group was readily checked from the infrared spectrum of the polymer (II), where an absorption band was observed at 738 cm^{-1} corresponding to $-(CH_2)_3-$ [18] as shown in Fig. 7, while the other two polymers, (I) terminated by tetra-n-butylammonium perchlorate and (III) obtained electrolytically in the presence of tetra-n-butylammonium perchlorate, had no absorption band due to butyl group. An absence of the butyl end group in both polymers, (I) and (III), was also supported by the NMR spectroscopic measurements of these polymers.

Identical results were obtained in the electroinitiated polymerization of styrene. Both polystyrene and tri-n-butylamine were obtained from the catholyte, although the molecular weight of polystyrene was higher than that of poly(α-methylstyrene).

Butadiene, Isoprene, and Chloroprene. The experimental results of the electroinitiated polymerization of butadiene, isoprene, and chloroprene are given in Table 2. From the catholyte, only low poly-

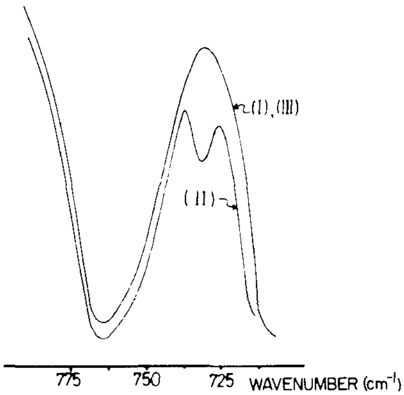


Fig. 7. Infrared spectra of poly(α-methylstyrene) terminated by tetrabutylammonium perchlorate (I), terminated by butyl iodide (II), electrolytically obtained polymer (III).

mers and tri-n-butylamine were obtained in the cases of polymerization of butadiene and isoprene. As in the electroinitiated polymerization of α-methylstyrene and styrene, these results suggest that the reaction in the cathodic compartment involved anionic propagation

Table 2. Polymerization of Butadiene, Isoprene, and Chloroprene[a]

Monomer[b]	Amount of current[c] $\times 10^{-3}$, F	Yield of the polymer, %
Butadiene	0.67	0.4
Butadiene	2.2	1.5
Butadiene	4.5	4.3
Isoprene	2.2	36
Isoprene	4.9	26
Chloroprene	2.2	Trace
Chloroprene	5.4	Trace
Chloroprene	4.5	3.0

[a] Conditions: 60 ml of dimethoxyethane containing 2.0 g of tetrabutylammonium perchlorate, polymerized at 30°C.

[b] Each run used 50 mmoles of the monomer.

[c] Current was 3 mA in each run.

and termination with the countercation. From the NMR spectrum of polybutadiene, which showed the presence of pentyl group due to signals at 8.7 and 9.0 ppm and methyl group attached to double bond at 8.4 ppm as shown in Fig. 8, it is also noticed that the termination

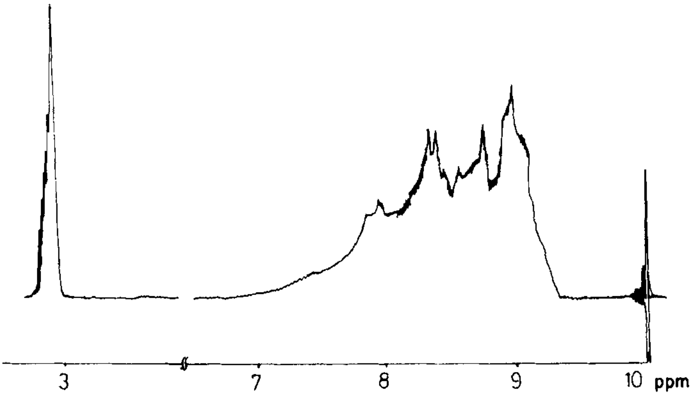


Fig. 8. 60 MHz NMR spectrum of polybutadiene. Solvent, benzene; concentration, ca. 10%; temp., room temp.; standard, TMS.

occurred by reaction with both butyl cation and proton. On the other hand, polyisoprene had no NMR signal corresponding to butyl group, supporting the termination by proton abstraction.

In the case of the electroinitiated polymerization of chloroprene as well as vinylidene chloride, low polymers were produced in the catholyte and tri-n-butylamine was not detected. The absence of tri-n-butylamine in the catholyte indicates that the growing chain end was not carbanion. From the infrared spectrum of polychloroprene, it was found that the polymer contained a high proportion of trans-1, 4 addition, as was observed in the polymer formed by radical initiators [19]. Although the polymerization of chloroprene and vinylidene chloride with anionic catalysts were reported [12, 20], there was no evidence of the anionic propagation of chloroprene, and anionic catalysts produced only colored low polymer of vinylidene chloride. In this study, therefore, the electroinitiated polymerization of each of the two monomers appears to proceed by the radical propagation rather than the anionic one.

Acrylonitrile. During the electrolysis of acrylonitrile, a viscous red deposit was observed around the cathodic electrode and the solution became yellowish red.

The catholyte was treated with methanol-HCl after electrolysis and dark yellow polymer was obtained. The yellow color of the polymer remained after reprecipitation with N, N-dimethylformamide-methanol system.

The infrared spectrum of polyacrylonitrile showed the absorption band at 740 cm^{-1} and tri-n-butylamine was detected by gas chromatography, implying the termination by abstraction of butyl cation. The abstraction of proton might be possible and the third possibility of termination is the deactivation of propagating end described by Szwarc [21].

Including these three terminations, the reaction scheme is proposed as follows:

"Electroinitiation":

$$M + e \longrightarrow M^{\ominus} \tag{5}$$

Anionic propagation:

$$\sim C^{\ominus} + M \xrightarrow{k_p} \sim C^{\ominus} \tag{6}$$

Chain transfer of anion to monomer:

$$\sim C^{\ominus} + M \longrightarrow \text{polymer} + M^{\ominus} \tag{7}$$

Termination with tetra-n-butylammonium ion:

$$\sim C^{\ominus} + Bu_4N^{\oplus} \begin{array}{ll} \xrightarrow{k_{t2}} \sim C\text{—}C_4H_9 + Bu_3N & (8) \\ \xrightarrow{k_{t3}} (\text{polymer})\text{—}H + C_4H_8 + Bu_3N & (9) \end{array}$$

Deactivation of propagating end:

$$\sim C^{\ominus} \xrightarrow{k_{t1}} \sim C^{\ominus\prime} \tag{10}$$

In the one-electron transfer from cathode to monomer [Eq. (5)], coupling of radical anions might follow, forming dianions. Successive two-electron transfer also might occur, giving dinegative ions [22]. These two initiation modes make no difference in the kinetic consideration. From Eqs. (5), (8), (9), and (10), the apparent rate of formation of the growing end is given by

$$d[M^{\ominus}]/dt = [I] - k_t[M^{\ominus}] \tag{11}$$

where [I] has units of F/liter-sec, and

$$k_t = k_{t1} + (k_{t2} + k_{t3})\,[Bu_4NClO_4] \tag{12}$$

Integrating Eq. (11),

$$[M^{\ominus}] = [I]/k_t \{1 - e^{-k_t \cdot t}\} \tag{13}$$

In analogy with the typical anionic polymerization of acrylonitrile [23], the rate of polymerization is given by

$$-d[M]/dt = k_p[M][M^{\ominus}] \tag{14}$$

Since $k_t \cdot t \gg 1$ could be assumed in the experimental condition, neglecting the second term in Eq. (13),

$$[M^{\ominus}] = [I]/k_t \tag{15}$$

Substituting this value into Eq. (14) and integrating this,

$$[M]/[M]_0 = \exp\{-[I]\, t \cdot k_p/k_t\} \tag{16}$$

The values of k_p/k_t, which are estimated from Eq. (16), are almost constant, as shown in Table 3. This suggests that the reaction scheme as proposed in the equations above [(5)-(10)] is reliable.

Table 3. Polymerization of Acrylonitrile[a]

No.	Monomer, mmoles	Current, mA	Amount of current $\times 10^{-4}$ F	Yield of polymer, %	$\overline{DP}$	k_p/k_t[b]
063	25	3	10.1	72	34	38
064	25	3	6.7	62	26	43
065	25	3	4.5	44	24	39
066	25	3	2.2	28	13	43
067	50	3	4.5	48	25	43
068	25	9	4.5	53	33	50

[a] Conditions: 60 ml of dimethoxyethane containing 2.0 g of tetra-n-butylammonium perchlorate, polymerized at 30°C.

[b] Calculated from Eq. (16).

Methacrylonitrile. Dark red polymethacrylonitrile was formed around the cathodic electrode by electroinitiated process. The produced polymer was treated as in the case of polyacrylonitrile. Tri-n-butylamine was detected by gas chromatography and no absorption band corresponding to the butyl group was observed in the infrared spectrum of the polymer, indicating termination by proton abstraction.

Experimental results are summarized in Table 4. When the concentration of the supporting electrolyte was increased, the yield and the molecular weight of the polymer decreased. The decrease of the yield is assumed to be caused by termination with supporting electrolyte: The higher the level of the electrolyte, the larger the value of k_t becomes, [Eq. (12)], and the yield decreases [Eq. (16)]. The fact that the molecular weight of the polymer was proportional to the concentration of the monomer, as shown in Fig. 9, indicates

Table 4. Polymerization of Methacrylonitrile[a]

No.	Monomer, mmoles	Current, mA	Amount of current $\times 10^{-4}$ F	Yield of polymer, %	$\overline{DP}$	k_p/k_t[b]
087	25	3	10	33	22	12
086	25	3	6.7	25	34	13
088	25	3	4.5	17	34	13
089	25	3	2.2	11	34	15
072	25	2	4.5	16	33	12
090	25	6	4.5	18	44	13
091	25	9	4.5	18	35	14
092	50	6	4.5	18	92	13
093	75	6	4.5	18	136	13
095[c]	50	6	4.5	24	148	18
097[c]	50	6	4.5	12	110	8
096[c]	50	6	4.5	9.5	99	7

[a] Conditions: 60 ml of dimethoxyethane containing 2.0 g of tetra-n-butylammonium perchlorate, polymerized at 30°C.

[b] Calculated from Eq. (16).

[c] Runs 095, 097, and 096 used 1.0, 4.0, and 6.0 g, respectively, of tetra-n-butylammonium perchlorate.

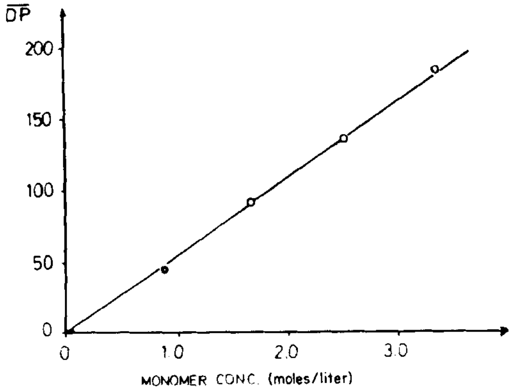


Fig. 9. Degree of polymerization of polymethacrylonitrile vs. monomer concentration.

the absence of chain transfer to the monomer [23]. From these results the reaction scheme seemed to be similar to that of acrylonitrile, exclusive of the transfer to the monomer and the termination by abstraction of butyl cation. Similar to acrylonitrile, the values of k_p/k_t could be calculated by Eq. (16); these values are almost constant, as shown in Table 4, except in the cases of high levels of the electrolyte.

When the polymerizations were conducted at highly negative values of the cathode potential, enough to reduce the supporting electrolyte (Fig. 10) and at a constant amount of current, the yield of the

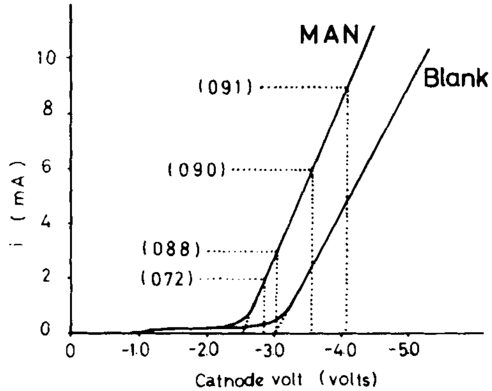


Fig. 10. i-V curves of methacrylonitrile (MAN) and tetrabutylammonium perchlorate (Blank) in dimethoxyethane. See also Table 4 and Fig. 11. Numbers in parentheses are the experimental numbers.

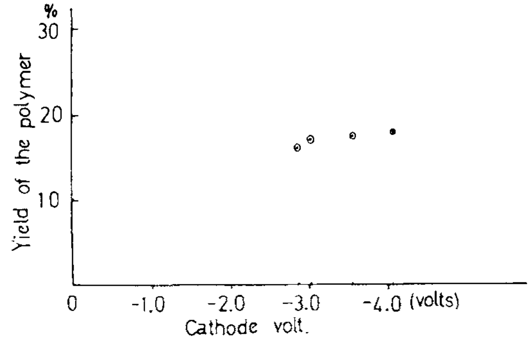


Fig. 11. Yield of polymethacrylonitrile vs. cathode potential. Amount of current, 4.5 × 10^{-4} F. See Fig. 10 and Table 4.

polymer was independent of the cathode potential, as shown in Fig. 11. This indicates that the current efficiency is not affected by the cathode potential. This type of behavior might be explicable if the preferential adsorption of the monomer occurs on the cathodic surface [24]. The supporting electrolyte could not attack the cathode because of the layer of the monomer on the surface, and hence electron is transfered to the monomer but not to the supporting electrolyte.

REFERENCES

[1] G. J. Parravano, *J. Am. Chem. Soc.*, **73**, 628 (1951).
[2] B. L. Funt and K. C. Yu, *J. Polymer Sci.*, **62**, 359 (1962).
[3] J. W. Breitenbach and Ch. Srna, *Pure Appl. Chem.*, **4**, 245 (1962).
[4] N. Yamazaki, S. Nakahama, and S. Kambara, *J. Polymer Sci.*, **B3**, 57 (1965).
[5] B. L. Funt, D. Richardson, and S. N. Bhadani, *Can. J. Chem.*, **44**, 711 (1966).
[6] B. L. Funt, S. N. Bhadani, and D. Richardson, *J. Polymer Sci.*, **(A-1)4**, 2871 (1966).
[7] B. L. Funt and S. N. Bhadani, *J. Polymer Sci.*, **C23**(1), 1 (1968).
[8] B. L. Funt and F. D. Williams, *J. Polymer Sci.*, **A2**, 865 (1964).
[9] D. Laurin and G. Parravano, *J. Polymer Sci.*, **B4**, 797 (1966).
[10] Y. H. Inami and J. B. Ramsey, *J. Chem. Phys.*, **31**, 1298 (1959).
[11] N. Kawabata, T. Tsuruta, and J. Furukawa, *Makromol. Chem.*, **51**, 70 (1962).
[12] A. Konishi, *Bull. Chem. Soc. Japan*, **35**, 395 (1962).

[13] T. Fueno, K. Asada, and J. Furukawa, *J. Polymer Sci.*, **40**, 511 (1959).
[14] T. Fueno, K. Asada, K. Morokuma, and J. Furukawa, *Bull. Chem. Soc. Japan*, **32**, 1003 (1959).
[15] M. Murphy, M. G. Carangelo, M. B. Ginaine, and C. Markham, *J. Polymer Sci.*, **54**, 107 (1961).
[16] S. Wawzonek, E. W. Blaha, R. Berkey, and M. E. Runner, *J. Electrochem. Soc.*, **102**, 235 (1955).
[17] H. L. Jackson and K. L. Seligmon, U.S. Pat. 3, 004, 012 (1961).
[18] G. Schnell, *Ber. Bunsenges. Physik. Chem.*, **70**, 297 (1966).
[19] R. C. Ferguson, *J. Polymer Sci.*, **A2**, 4735 (1964).
[20] K. W. Wilson, F. E. Anderson, and R. W. Donohoe, *Anal. Chem.*, **23**, 1032 (1951).
[21] M. Szwarc, *Advan. Polymer Sci.*, **2**, 275 (1960).
[22] M. M. Baizer, *Tetrahedron Letters*, **1963**, 973.
[23] A. Zilkha, B. A. Feit, and M. Frankel, *J. Polymer Sci.*, **49**, 231 (1961).
[24] N. Sato, K. Sugino, and T. Sekine, *Electrochem. Technol.*, **1**, 112 (1963).

Accepted by editor June 18, 1968
Received for publication July 29, 1968