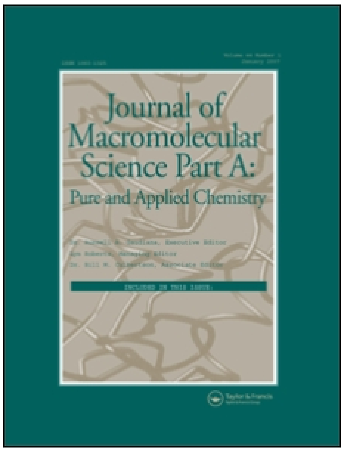

Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Termination Mechanism in the Anionic Polymerization of Methyl Methacrylate

R. P. Chaplin[a]; Sena Yaddehige[a]
[a] School of Chemical Technology University of New South Wales, Kensington, Australia

To cite this Article Chaplin, R. P. and Yaddehige, Sena(1980) 'Termination Mechanism in the Anionic Polymerization of Methyl Methacrylate', Journal of Macromolecular Science, Part A, 14: 1, 23 — 31

To link to this Article: DOI: 10.1080/00222338008063206

URL: http://dx.doi.org/10.1080/00222338008063206

J. MACROMOL. SCI.–CHEM., A14(1), pp. 23-31 (1980)

Termination Mechanism in the Anionic Polymerization of Methyl Methacrylate

R. P. CHAPLIN and SENA YADDEHIGE

School of Chemical Technology
University of New South Wales
P. O. Box 1
Kensington, N. S. W. 2033, Australia

ABSTRACT

Recent studies have revealed that at temperatures around 200°K in tetrahydrofuran solvent, poly(methyl methacrylate) ion pairs are long-lived and very reactive. At higher temperatures however termination of the ion pairs occurs, as evidenced by the broadening of the molecular weight distribution of the resultant polymer and by the incomplete polymerization of the monomer. Three mechanisms have been proposed to describe these termination reactions; an intermolecular reaction with the monomer ester function, an intramolecular cyclization of the anion, or reaction with the polymer ester function. In the absence of monomer only the last two mechanisms can be operative. A series of experiments was undertaken in which the molecular weight distribution broadening with temperature increase was measured under typical polymerization conditions or in the absence of monomer. The effect of each of the three counterions Li, Na, and K was also monitored. The results obtained are discussed in terms of these three possible termination mechanisms. Termination rate constants calculated from the molecular weight distribution are also presented.

INTRODUCTION

Although recent studies have produced accurate rate data for the anionic polymerization of methyl methacrylate (MMA) at low temperatures [1, 2], higher temperature studies have proven less rewarding due to the instability of the carbanions at these temperatures [3].

In studies of the polymerization of MMA by Grignard reagents at 273° K in toluene, Owens et al. [4] and Goode et al. [5] reached the same conclusion that termination reactions of the polymerizing center invariably resulted in the formation of a cyclic β-keto ester. This ester represented about 3% of the overall yield. Although we now know [6] that polymerization of MMA by Grignard reagents proceeds by a coordination rather than an anionic mechanism the production of this ester as a side product is significant.

Glusker and his associates [7] proposed a pseudo-termination reaction to explain the vagaries of the polymerization of MMA initiated by fluorenyllithium in a toluene/diethyl ether solvent. This reaction involved the initial formation of a cyclic trimer which added monomer very slowly while retaining its cyclic structure. The elimination of lithium methoxide to produce a cyclic ketone was a true termination reaction which at 273° K proceeds rapidly, while at 210° K the reaction was much slower.

Rempp et al. [8] have reported that in THF at 290° K termination of MMA anions occurs rapidly at room temperature if excess monomer is present while in the absence of monomer the MMA anions are stable. This result led to the conclusion that at 290° K termination occurs by attack of the carbanion on the monomer ester function, a reaction previously proposed by Schreiber [9]. A similar attack on the polymeric ester groups was not observed.

Wiles and Bywater [10] accounted for the concomitant production of methoxide ions in the anionic polymerization of MMA with 1,1-diphenylhexyllithium as initiator by proposing a ring-closure reaction of a cyclic intermediate of similar structure to that proposed by Glusker [7]. The addition of monomer to such a carbanion has also been postulated [11] to account for the stereospecificity of the anionic polymerization of MMA, especially in toluene with a lithium counterion. The closure of the ring is thus a naturally accepted mechanism to explain termination reactions of the carbanion that under other conditions can be quite stable.

Lohr [12] and Schulz et al. [13] were able to obtain values for the rate of termination of MMA-cesium ion-pairs in THF by assuming that such termination is caused exclusively by reaction of these ion-pairs with the ester function of MMA monomer, an assumption already foreshadowed by Rempp [8].

From all these studies it is apparent that the mechanism of termination is well documented without any direct proof offered to show which mechanisms are more important in a polymerization system. With the introduction of GPC as a reliable mechanistic tool it is now

TABLE 1. Proposed Termination Reactions of the Polymethylacrylate Ion Pair and their Effect on the MWD of the Resultant Polymer

	Effect on MWD	
Termination reaction	In presence of monomer	In absence of monomer
With solvent	Broaden	Unchanged
With monomer	Broaden	-
With polymer	Broaden	Broaden
By intramolecular cyclization	Broaden	Unchanged

possible to examine these proposed termination mechanisms from molecular weight distribution (MWD) data of the polymers formed under various conditions. Table 1 is a summary of the various reactions and indicates what information can be expected from analyses by GPC.

It was thus the purpose of this paper to investigate more fully the mechanism of termination as well as extending the kinetic data to include the counterions Li, Na, and K.

EXPERIMENTAL

The purification procedures and MWD determination by GPC were as reported in a previous paper [2].

All experiments were carried out in THF in the presence of 2×10^{-3} $\underline{M}$ of the appropriate salt, i. e., Li, Na tetraphenyl boride, or K-cyanotriphenyl boride.

All initiators were prepared by the standard technique of contacting the appropriate material with the metal, with the necessary precautions being observed to ensure that no side reactions occurred.

The termination reactions of the MMA anions were investigated in the presence (type I conditions) and absence (type II conditions) of monomer.

Type I Polymerization Conditions

The procedure of double initiation was used whereby the PMMA chain was initiated at 200°K, after which the temperature of the solution was rapidly raised to the polymerization temperature and monomer added. After 30 min, methanol was added to terminate the polymerization. The polymer was isolated and its MWD determined.

TABLE 2. Termination Reactions of Poly(methyl Methacrylate) Ion Pairs in THF with Type II Polymerization Conditions: MW Data of Resultant Polymers

Initiator	Method[a]	M_n from GPC	PDI	Remarks
Sodium naphthalene	a	42,500	1.19	Control polymerized at 200°K
	b	52,300	1.32	12 hr at 250°K
	c	40,200	1.29	No polymerization of second monomer
Fluorenylsodium	a	49,300	1.07	Control at 200°K
	b	25,800	1.20	12 hr at 250°K
	c	40,000	1.20	Approximate calculations from bimodal GPC
		120,000	1.20	
Fluorenyllithium	a	30,000	1.15	Control at 200°K
	b	52,000	1.28	12 hr at 250°K
	c	80,000	1.31	No polymerization of second monomer
Potassium	a	51,400	1.34	Control at 200°K
α-methylstyrene dimer	c	33,000	-	Approximate calculations bimodal GPC
		80,000	-	

[a] See Experimental Section.

Type II Polymerization Conditions

After forming the "living" chain at 200°K the temperature of the solution was raised to 250°K and held for 12 hr, after which methanol was added (method b, Table 2). In some experiments (method c) the solution was recooled to 200°K and a second batch of monomer added after which the polymer was isolated and its MWD determined. In control experiments (method a) the living chain was formed at 200°K.

RESULTS AND DISCUSSION

The results for the termination reactions in the absence of monomer are shown in Table 2. Although some broadening in the MWD occurred with all counterions after 12 hr at 250°K, indicating some reaction of the anion with the polymer ester function had occurred, the rate was considered to be very slow. Only with the two initiators fluorenylsodium and potassium α-methylstyrene dimer did polymerization of the second monomer occur, the termination rate with the other two initiators being more rapid. The fundamental difference between the two initiators with sodium as the counterion is puzzling, but the fact that with fluorenylsodium the solution remains colored throughout the polymerization suggests that a more complex propagation mechanism than a simple anionic one is operating.

In the presence of monomer, type I conditions, with fluorenylsodium as the initiator, the MWD increased slowly but significantly with temperature. These results are shown in Table 3. With a similar experiment carried out at 230°K with sodium naphthalene as initiator, 100% polymerization was achieved, and the resultant polymer had a MWD of 1.40.

With fluorenylpotassium as initiator, the surprising result obtained was that the MWD did not change significantly with temperature. As with fluorenylsodium, the polymerization solution also remained colored until termination occurred.

Treatment of Results

In order to analyze the results from type I polymerization conditions two models were used. The first was devised by Lohr [12] and uses the simple kinetic scheme shown in Eqs. (1):

$$\begin{aligned} M_n^-, \text{Me} + M &\xrightarrow{k_p} \sim\!\sim\!\sim M_{n+1}, \text{Me} \\ &\xrightarrow{k_t} \sim\!\sim\!\sim M_n{-}M + \text{MeOR} \end{aligned} \tag{1}$$

TABLE 3. Termination Reactions of Poly(methyl methacrylate) Ion Pairs in THF with Type I Polymerization Conditions: MW Data of Resultant Polymers

Initiator	M_n from GPC	PDI	X_p (%)	Temperature of polymerization (°K)
Fluorenylsodium	60,500	1.15	100	200
	40,500	1.35	100	220
	18,000	1.42	70	245
	19,000	1.47	42	256
Fluorenylpotassium	140,000	1.50	100	200
	86,500	1.67	98	220
	36,000	1.64	98	245
	54,000	1.53	97	256
	29,000	1.71	92	270

where k_p is the rate constant for propagation of MMA ion pairs and k_t is the termination rate constant.

A second possible model was proposed by Szwarc [14]. This model was proposed in order to examine the effect on the resultant polymer MWD of the continuous addition of monomer to a living anion, the monomer containing a mole fraction f of impurities which would terminate some of these anions. In the adaption to our case, f would be simply given by the expression (2):

$$f = k_t/(k_t + k_p) \qquad (2)$$

The resultant expressions for the polydispersity index (PDI), i. e., the ratio of weight-average to number-average MW, is given in Eqs. (3) and (4) respectively.

Lohr:

$$\mathrm{PDI} = (2/(\alpha X_p)^2 [\alpha X_p + (1 - \alpha X_p)\ln(1 - \alpha X_p) - (U_i/2)\ln(1 - \alpha X_p)^2] \qquad (3)$$

Szwarc:

$$\mathrm{PDI} = (2/\alpha 2)\ [\alpha + (1 - \alpha)\ln(1 - \alpha)] \qquad (4)$$

where

$$= K[M]_0/[I]_0$$

$$K = k_t/(k_p + k_t)$$

and X_p = fractional conversion and U_i = internal nonuniformity of the living polymer before termination. An approximate value of $U_i = 0$ was chosen for the calculations.

From the results seen in Table 2 for type II conditions it is apparent that termination occurs by a simple first-order intramolecular process as indicated by Eq. (5)

$$M_{n'}\text{-Me} \xrightarrow{k_t} M_n + \text{MeOR} \tag{5}$$

Although intermolecular termination is also occurring as evidenced by the slight broadening of the MWD after 12 hr at 250°K, the rate is considered to be very slow at this temperature.

The termination rate constants k_t were calculated where possible from the relation (6):

$$\ln[\overline{M}_n(2)/\overline{M}_n(1)] = k_t t \tag{6}$$

where $\overline{M}_n(1)$ and $\overline{M}_n(2)$ are the number-average molecular weights of the original polymer and of the polymer produced by the addition of the second batch of monomer, respectively. In those cases where no polymerization of the second monomer occurred only a minimum rate constant could be estimated.

The results of the applications of these models to type I and type II polymerization conditions are shown in Table 4.

The values of the termination rate constants for type I conditions have been calculated by using the model proposed by Lohr. Use of the modification of the Szwarc model only produces a small difference, a difference which is certainly within the experimental errors associated with the determination of the MW data.

Whilst the errors associated with these results will be quite large, it is significant that the rate of intramolecular cyclization is much lower than the rate of termination of the anions by reaction with the monomer ester function at 250°K, both of which are very much less than the propagation rate constants.

It is apparent from these results that the most important termination reaction in a PMMA system undergoing polymerization is the reaction of the ion pair with the ester function of the MMA monomer,

TABLE 4. Rate Constants for Termination of Poly(methyl Methacrylate) Ion Pairs in THF for Type I and Type II Conditions

Condition	Initiator	k_t[a]	Temperature (°K)
Type I	Fluorenylsodium	0.03	200
		0.11	250
	Fluorenylpotassium	0.18	200
		0.18	250
Type II	Sodium naphthalene	$> 10^{-3}$	250
	Fluorenylsodium	2.5×10^{-5}	250
	Fluorenyllithium	$> 10^{-3}$	250
	Potassium α-methylstyrene	2×10^{-5}	250

[a] k_t in liter/mole-sec for type I conditions and in sec^{-1} for type II conditions.

the rate constant for this reaction being many orders of magnitude larger than self-termination reactions of the ion pair itself.

There is some circumstantial evidence that this self-termination reaction of the ion pair occurs by an intramolecular cyclization reaction, for examination of a model proposed for such a complex indicates that such a reaction would be expected to proceed much faster with the smaller Li cation than with the larger K cation as was indeed the case.

A more extensive examination of this proposal is needed, however, and is being undertaken in our laboratories at this time.

ACKNOWLEDGMENT

The authors thank the Australian Research Grants Committee for support of this work.

REFERENCES

[1] G. Lohr and G. V. Schulz, Eur. Polym. J., 10, 121 (1974).
[2] R. P. Chaplin, S. Yaddehige, and W. Ching, Eur. Polym. J., 15, 5 (1979).

[3] P. E. M. Allen, R. P. Chaplin, and D. O. Jordan, Eur. Polym. J., 8, 271 (1972).

[4] F. H. Owens, W. L. Myers, and F. E. Zimmerman, J. Org. Chem., 26, 2288 (1961).

[5] W. E. Goode, F. H. Owens, and W. L. Myers, J. Polym. Sci., 47, 75 (1960).

[6] P. E. M. Allen and B. O. Bateup, JCS Faraday Trans. I, 71, 2203 (1975).

[7] D. L. Glusker, I. Lysloff, and E. Stiles, J. Polym. Sci., 49, 315 (1961).

[8] P. Rempp, V. I. Volkov, J. Parrod, and C. Sadron, Bull. Soc. Chim. France 1960, 1919.

[9] H. Schreiber, Makromol. Chem., 36, 86 (1959).

[10] D. M. Wiles and S. Bywater, Trans. Faraday Soc., 61, 150 (1965).

[11] W. Fowells, C. Schuerch, F. A. Bovey, and F. P. Hood, J. Am. Chem. Soc., 89, 1396 (1967).

[12] G. Lohr, Makromol. Chem., 172, 151 (1973).

[13] G. Lohr, A. H. E. Muller, V. Warzelhan, and G. V. Schulz, Makromol. Chem., 175, 497 (1973).

[14] M. Szwarc and M. Litt, J. Phys. Chem., 62, 568 (1958).