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

Anionic Polymerization of Methyl Methacrylate in the Presence of Piperidine

A. Kolá[a]; J. Trekoval[a]; P. Vlĉek[a]
[a] Institute of Macromolecular Chemistry Czechoslovak Academy of Sciences 162 06, Prague, Czechoslovakia

To cite this Article Kolá, A. , Trekoval, J. and Vlĉek, P.(1978) 'Anionic Polymerization of Methyl Methacrylate in the Presence of Piperidine', Journal of Macromolecular Science, Part A, 12: 5, 757 — 768
To link to this Article: DOI: 10.1080/00222337808066590
URL: http://dx.doi.org/10.1080/00222337808066590

J. MACROMOL. SCI.–CHEM., A12(5), pp. 757-768 (1978)

Anionic Polymerization of Methyl Methacrylate in the Presence of Piperidine

A. KOLÁŘ, J. TREKOVAL,* and P. VLČEK

Institute of Macromolecular Chemistry
Czechoslovak Academy of Sciences
162 06 Prague 6, Czechoslovakia

ABSTRACT

Anionic polymerization of methyl methacrylate (MMA) initiated by lithium tert-butoxide (t-BuOLi) was investigated in different mixtures of benzene and piperidine. The latter compound activates the associated alkoxide, as evidenced by the observed increase in the rate of polymerization, proportional to piperidine concentration and also by the lowering of the overall kinetic order of the polymerization reaction with respect to initial monomer concentration. However, at higher piperidine concentration the rate of the polymer growth significantly decreases after a short period of time; a probable reason for this retardation or termination effect is the decay of active growth centers by a termination reaction with the methacrylate carbonyl group. The molecular weight of the polymer is significantly lowered by even a small addition of piperidine as a result of increased initiator efficiency that leads to a higher absolute concentration of active centers and approaches the theoretical limit given by the stoichiometric ratio of monomer and initiator concentrations. The microstructure of the product is affected by the presence of the polar solvent to a considerably lesser degree than in the case of classical alkylmetal initiators. The isotacticity slowly

*Author to whom all correspondence should be addressed.

decreases with piperidine concentration over the whole investigated range. The high stability of the complex active center of growth formed by the alkoxide initiator and also the gradual change in the character of the ionic pair at the end of the growing polymer chain are responsible for the relatively small changes of the microstructure.

INTRODUCTION

Linear as well as cyclic amines and ethers, commonly employed as polar solvents in the anionic polymerization of methacrylates, significantly influence both the kinetics of polymerization and the properties of the polymer formed. They affect the rate of polymerization by solvation and simultaneously change the stereospecific efficiency of the active centers of growth in such a way that polymers having a considerably lower content of the isotactic component are formed if the polymerization is initiated by organometallic lithium compounds than in the case of a medium of nonpolar hydrocarbons. In principle, the same effect of these solvating solvents is observed if the polymerization is initiated by lithium tert-alkoxides. In a nonpolar medium, alkoxides form active polymerization centers; these are protected by inactive alkoxide (alkoxide which has not participated in the initiation reaction) to such an extent that they are capable of functioning for a sufficiently long period of time even at room temperature and, on the other hand, give rise to a polymer with a higher isotacticity than the classical alkylmetals [1]. This is due to the strong complex character of the growing chain ends and also to the fact that their possible termination with the carbonyl group of the monomer or polymer is blocked [2]. However, a change in the solvation properties of the reaction medium, due to the addition of a polar solvent or to an increased polarity of the monomer itself, can interfere with the function and/or existence of this complex [3-5]. Accordingly, changes in the polymerization kinetics and/or in the microstructure of the polymer can be considered as a qualitative measure of the stability of the complex active center generated from the living chain end and the molecules of alkoxide that has not reacted in the initiation stage.

In this communication we continue our study of the polymerization of methacrylate esters initiated by alkali metal tert-alkoxides; the paper is devoted to the polymerization of methyl methacrylate (MMA) initiated by lithium tert-butoxide (t-BuOLi) in the presence of piperidine.

EXPERIMENTAL

Reagents

MMA, benzene, t-BuOLi purification and preparation were as already described, as was the polymerization technique in dilatometers under argon [1].

Piperidine (Reachim, U. S. S. R.) was dried by BaO and distilled twice on a column (bp 106°C, atmospheric pressure); only the middle fraction was always taken (about 50%). Just before polymerization the necessary amount was dried for 24 hr by CaH_2, which was removed immediately before use by centrifugation [6].

Methods

The polymer microstructure was determined from NMR spectra measured on a JEOL-100 spectrometer and evaluated in a standard manner [7]. The molecular weights were determined either by viscometry in benzene and calculated from the relevant Mark-Houwink equation [8]

$$[\eta] = 5.7 \times 10^{-5} M^{0.76}$$

or by means of GPC in tetrahydrofuran as described elsewhere [9]; for the evaluation of chromatograms the equation [10]

$$[\eta] = 1.08 \times 10^{-4} M^{0.702}$$

was employed.

RESULTS

The course of methyl methacrylate polymerization initiated by lithium tert-butoxide with different amounts of piperidine added is presented in Figs. 1 and 2; the polymerization conditions are summarized in Table 1. It is seen that the initial rate of polymerization increases with increased piperidine concentration, but before quantitative conversion is reached, a change of slope occurs on the conversion curves and the polymerization rate sharply decreases. Both the time and conversion that correspond to this inflection are inversely proportional to the piperidine concentration in the reaction mixture (Fig. 1 and Table 1); the initial rate of polymerization increases

TABLE 1. Effect of Piperidine on Anionic Polymerization of Methyl Methacrylate Initiated by t-BuOLi[a]

No.	Piperidine (mole/liter)	Conversion (%)	R_p (mole/liter-sec)	Tacticity I (%)	Tacticity H (%)	Tacticity S (%)	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
B5	-	38	4.45	76.2	15.9	7.9	290	140	2.09
P1	0.0467	35	6.14	78.9	14.4	6.7	117	56	2.09
P7	0.467	33	7.57	74.7	16.5	8.8	62	25	2.45
P2	0.975	33	13.82	72.0	17.2	10.8	58	28	2.09
P3	1.870	29	20.22	67.5	19.8	12.7	47	24	1.94
P4	3.740	22	29.00	61.4	22.5	16.1	-[b]	-	

[a]MMA = 467 mole/liter; t-BuOLi = 0.0467 mole/liter.
[b]Below the sensitivity limit of the method.

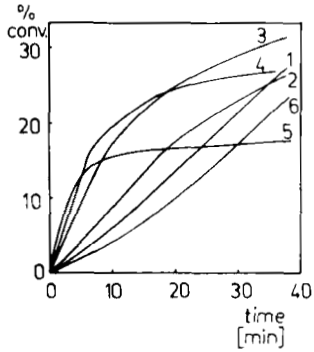

FIG. 1. Conversion curves in methyl methacrylate polymerization in the presence of various concentrations of piperidine: Monomer concentration: 4.67 mole/liter; initiator concentration: 0.047 mole/liter; (1) 0.047 mole/liter; (2) 0.467 mole/liter; (3) 0.935 mole/liter; (4) 1.870 mole/liter; (5) 3.740 mole/liter; (6) no piperidine.

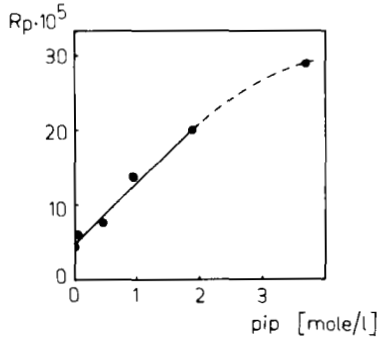

FIG. 2. Initial rate of polymerization as a function of piperidine concentration. Monomer concentration, 4.67 mole/liter; alkoxide concentration, 0.0467 mole/liter.

linearly with the concentration of piperidine practically over the whole range investigated (Fig. 2). The small deviation from this linear dependence at the highest piperidine concentration could be explained by an experimental error associated with the measurement of an extremely high reaction rate; however, it is also possible that at a high concentration of the solvating solvent all initiator molecules are utilized in the formation of active centers of growth and

practically no active centers with a protective complex are present, which could be affected by piperidine. As a result, the gradient of reaction rate drops when the piperidine concentration is further increased.

As expected, the mean molecular weights of polymers prepared under these conditions decrease with increasing piperidine concentration. However, this decrease is not linear within the investigated concentration range. At first, the molecular weight decreases very steeply in the region of piperidine concentrations that are comparable with the concentration of the initiator but remain nearly constant when the concentration of the solvating compound is further increased (Table 1 and Fig. 3). At a high concentration of piperidine (experiment P4 in Table 1), the molecular weight of the product was very low and could not be measured by the two methods employed; presumably it was lower than 2×10^4, the lower resolution limit of the GPC set. The microstructure of the polymer prepared in the benzene-piperidine mixture is characterized by a decrease in isotacticity with piperidine concentration (Table 1 and Fig. 4); this decrease is, however, much less pronounced than in similar polymerizations initiated by alkylmetal initiators of the type R-Li.

As there existed a possibility of a contingent deactivation of the initiator by piperidine, a number of polymerizations were carried out in the following way: a mixture of given amounts of alkoxide and piperidine was intentionally left to stand in the dilatometer, and only after different time intervals (τ in Table 2) the monomer was added. The results show that within the time interval investigated neither the rate of polymerization nor the microstructure or molecular weight is influenced.

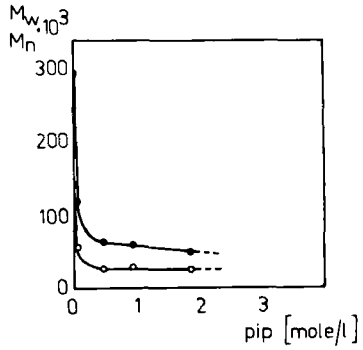

FIG. 3. Dependence of polymer molecular weight on piperidine concentration: (○) $\bar{M}_n$; (●) $\bar{M}_w$. Monomer concentration, 4.67 mole/liter; initiator concentration, 0.047 mole/liter.

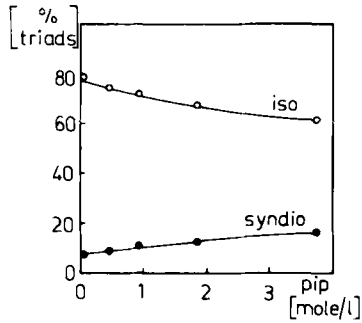

FIG. 4. Dependence of polymer microstructure on piperidine concentration in the polymerization mixture. Monomer concentration, 4.67 mole/liter; initiator concentration, 0.047 mole/liter.

The overall reaction order of the polymerization with respect to the initial monomer concentration was determined in a series that covered the range of MMA concentrations between 1.4 and 6.54 mole/liter and was found to be about 2, a decrease by one in comparison with a similar polymerization carried out in a hydrocarbon medium [1].

DISCUSSION

As pointed out earlier [3], the probable reason for the long lifetime of active centers in the methyl methacrylate polymerization initiated by lithium tert-butoxide is the existence of a protective envelope of the growing chain ends. This protective cover is formed by alkoxide that has not reacted in the initiation step. The results of this communication show that piperidine can lower the possibility of formation of these protected centers in such a way that within a relatively short time period the rate of polymerization is significantly decreased and, at higher concentrations of piperidine the growth can be suddenly terminated. It can be assumed that the nonprotected active conter reacts in the known way with the ester groups of the monomer or polymer and yields inactive products [11]. On the other hand, the fact that the overall polymerization rate is second-order with respect to the initial monomer concentration (see above) indicates that piperidine participates in the initiation step. If we assume that the initiation of methyl methacrylate polymerization by lithium tert-butoxide in a nonpolar, hydrocarbon medium is a two-step reaction between the monomer and alkoxide (second-order with respect to the initial monomer concentration), we can

TABLE 2. Rate of Polymerization and Polymer Microstructure in Dependence on the Time of Interaction between Piperidine and Initiator[a]

No.	Time (min)	$R_p \times 10^4$ (mole/liter-sec)	Microstructure		
			I (%)	H (%)	S (%)
P5	1.5	7.25	74.0	17.0	9.0
P6	6.5	7.27	73.8	17.4	8.8
P7	13	7.57	74.7	16.5	8.8
P8	62	6.95	76.8	15.3	7.9
P9	130	7.87	74.2	16.1	9.7

[a]MMA = 4.67 mole/liter; t-BuOLi = 0.0467 mole/liter; piperidine = 0.467 mole/liter.

infer that in the initiation step the monomer is partially replaced by piperidine. Most probably, this reaction takes place in the alkoxide activation; the products of this activation then react with the monomer and give rise to the actual active centers of growth.

The increase of the rate of polymerization with piperidine concentration is almost linear within the measured range; this indicates that the number of active centers gradually rises as a result of dissociation and activation of alkoxide by piperidine. However, the increasing concentration of active centers may not be the only reason for the enhanced rate of polymerization. This is apparent from the shape of conversion curves in Fig. 1 and also from the decrease of mean molecular weight of polymers with piperidine concentration (Fig. 3): the molecular weight averages drop sharply only at low piperidine concentration and then remain practically constant. Even if we take into consideration that the useful separation range of the GPC column set employed ends at the lower limit of about $\overline{M}_w = 2 \times 10^4$, the decrease of both $\overline{M}_w$ and $\overline{M}_n$ is still very strong in the range of the ratio of piperidine to alkoxide concentrations of 0-2, and the molecular weight approaches the theoretical limit (1×10^4) given by concentration conditions. One can therefore conclude that the initiator is practically quantitatively utilized at piperidine concentrations equal to or only slightly higher than the concentration of alkoxide, and that a further rise of polymerization rate by this mechanism is no longer possible. Nevertheless, the rate of polymerization continues to increase and reaches a value

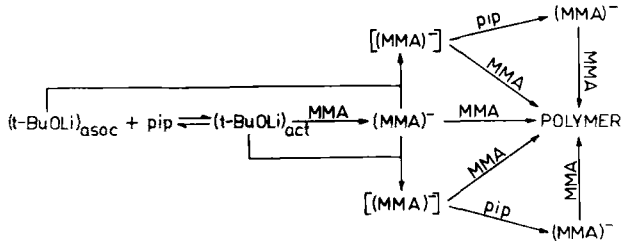

FIG. 5. Assumed reaction scheme in the system methyl methacrylate-piperidine-lithium tert-butoxide. $(MMA)^-$ denotes nonprotected active center of growth; $[(MMA)]^-$ denotes protected active center.

several times higher than the initial one (Fig. 2). This can be explained by the assumption that the character of active growth centers changes in a continuous manner as a function of the piperidine concentration. An attempt to visualize these processes is presented schematically in Fig. 5. In a hydrocarbon medium alkoxide is present in the form of inactive associates that can be solvated by added piperidine under the formation of the active initiator. This activated alkoxide then reacts either directly with the double bond of the monomer to yield the active center or with the previously formed oligomer chain which is then partially protected similarly as in the case of inactive alkoxide in a nonpolar, hydrocarbon medium. The probability of the latter reaction would probably decrease with concentration of piperidine so that the relative amount of active centers deprived of the protective complex would increase. As the growth is considerably quicker on these centers, the overall polymerization rate would rise. However, these centers easily undergo a termination reaction with the ester groups of the monomer or polymer so that with increasing piperidine concentration the lifespan of active growth centers decreases, and in this way the growth is terminated within a shorter period of time and at a lower conversion. It is also possible that the active centers are partially protected by associates of alkoxide, as their dissociation brought about by the solvent or monomer is reversible. With increasing piperidine concentration the corresponding equilibrium would be shifted towards the products of dissociation, and as a result of a lowered concentration of associates the possibility of their interaction with active centers formed would also decrease. In addition, it can be assumed that at higher concentrations of piperidine the active centers previously protected by the remaining associates of alkoxide could be decomposed by excess piperidine with the resulting

TABLE 3. Polymerization of MMA in Solvents of Different Solvating Power

MMA (mole/liter)	Solvent[a]	Solvent concn. (mole/liter)	Initiator	Initiator concn (mole/liter)	Conversion (%)	Microstructure		
						I (%)	H (%)	S (%)
8.87	Tol		t-BuOLi	0.086	28	81	13	6
1.81	"		"	0.097	23	83	12	5
2.80	"		"	0.025	19	82	13	5
1.88	MIB	1.76	"	0.011	58	82	13	5
4.74	"	3.08	"	0.024	29	80	14	6
1.86	BIB	1.21	"	0.011	49	84	12	4
4.68	THF	4.40	"	0.050	11	58	21	21
4.67	PIP	1.87	"	0.047	29	67	20	13
4.67	"	3.74	"	0.04	22	61	23	16
8.45	Tol		n-BuLi	0.045	30	52	25	23
0.10	"		"	0.012	22	71	17	12
0.74	MIB	2.77	"	0.022	100	29	30	41
0.93	THF	0.86	"	0.005	40	17	36	47
0.93	"	3.69	"	0.005	65	10	34	56
1.00	PY	1.05	"	0.06	88	9	35	56[b]
1.00	PY	5.47	"	0.06	88	8	31	61[b]

[a]Solvents Tol = toluene, MIB = methyl isobutyrate; BIB = butyl isobutyrate; THF = tetrahydrofuran; PIP = piperidine, PY = pyridine.

[b]See ref. 10.

exposure of the growing polymeric anion. In this way the relative amount of unprotected active centers would also increase with all the consequences. The assumption of a continuous change in the character of active centers is also corroborated by the fact that a parallel, continuous change of the microstructure of the product (the stereospecific efficiency of active centers) with increasing piperidine concentration is observed (Fig. 4). This specific feature of the alkoxide initiators has already been described and differs considerably from the stereospecific efficiency of alkyllithium in media of different solvating power: a pronounced lowering of isotacticity of polymers prepared by means of alkyllithium was observed, brought about by a very small amount of a similar electron-donor solvent (pyridine); a further increase in the solvating power of the polymerization medium did not influence the microstructure of the product [12]. This indicates that the active growing center formed by the reaction of the monomer with lithium tert-alkoxide has a more complex character and is stronger than that formed from the classical alkylmetal initiators (see Table 3). It can be assumed that the presence of piperidine as a solvent with a high solvating power does not change totally and quantitatively the character of centers formed in the initiation by alkoxides (in contrast to those formed in the initiation by alkylmetals). The changes in activity and stereospecific efficiency of growing centers strongly depend on concentration conditions. A drop in molecular weight of prepared polymers is observed only at catalytic concentrations of piperidine and is probably due to the activation of alkoxide associates by piperidine and thus to the increase of the efficiency of the initator to its quantitative utilization.

REFERENCES

[1] J. Trekoval and D. Lim, J. Polym. Sci. C, 4, 333 (1963).
[2] J. Trekoval, J. Polym. Sci. A-1, 9, 2575 (1971).
[3] J. Trekoval, Collect. Czechoslov. Chem. Commun., 42, 1529 (1977).
[4] J. Trekoval, P. Vlček, and D. Lim, Collect. Czechoslov. Chem. Commun., 36, 3032 (1971).
[5] P. Vlček and J. Trekoval, Makromol. Chem., 176, 2595 (1975).
[6] D. D. Perrin, W. L. Armarego, and D. R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, Oxford 1966, p. 242.
[7] F. A. Bovey and G. V. D. Tiers, J. Polym. Sci., 44, 173 (1960).
[8] G. l'Abbe and G. Smets, J. Polym. Sci. A-1, 5, 1359 (1967)
[9] J. Janča, P. Vlček, J. Trekoval, and M. Kolinský, J. Polym. Sci. Polym. Chem. Ed., 13, 1471 (1975).

[10] Z. Grubisic, P. Rempp, and H. Benoit, J. Polym. Sci. B, 5, 753 (1967).
[11] J. Trekoval and P. Kratochvíl, J. Polym. Sci. A-1, 10, 1391 (1972).
[12] D. Braun, M. Herner, U. Johnsen, and W. Kern, Makromol. Chem., 51, 15 (1962).

Accepted by editor September 5, 1977
Received for publication December 10, 1977