3038 *Macromolecules* **1996,** *29,* 3038−3039

Living Anionic Polymerization of Methyl Methacrylate at Ambient Temperatures in the Presence of the Tetraphenylphosphonium Cation

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Received September 19, 1995

Revised Manuscript Received January 29, 1996

In the last decade, great interest has emerged in the study of the polymerization of methyl methacrylate (MMA) under ambient conditions, primarily as a result of the development of the so called group-transfer polymerization (GTP) of MMA by Webster et al.[1] Several new polymerization systems for this monomer have been reported.[2] We now wish to report that the anionic polymerization of MMA in THF at ambient temperature in the presence of the tetraphenylphosphonium cation (Ph_4P^+) produces high molecular weight poly(methyl methacrylate) (PMMA, DP ≤ 500) in high yields with narrow molecular weight distributions (MWD ≤ 1.2).[3] Seebach et al. have reported similar results using an organic cation (a protonated phosphazene base, DP ≤ 222, MWD = 1.18),[4] and Reetz et al. have reported the anionic synthesis in unknown yield of a low molecular weight narrow MWD PMMA (MWD = 1.17, DP = 20) using the tetrabutylammonium cation (n-Bu_4N^+).[5] Webster et al. have also reported that the anionic polymerization of MMA (at 25−60 °C) with Bu_4N^+ and the hexabutylguanidinium ($[Bu_2N]_3C^+$) cation in the presence of silyl ethers gives narrow MWD PMMA (M_n = 9510, MWD = 1.77, and M_n = 5300, MWD = 1.44, respectively), but the yields were not quantitative.[6] Other anionic MMA polymerization systems capable in varying degrees of producing narrow MWD PMMA at ambient temperatures include ligand-modified,[7,8] crown-ether promoted,[9] "screened",[10] "high-speed immortal",[11] and "coordination",[12] polymerizations.

The early work reported by Reetz et al.[5] on metal-free anionic polymerization of n-butyl acrylate prompted us to explore the feasibility of anionic polymerizations of MMA in the presence of organic cations. Quirk et al. reported that the n-Bu_4N^+ salt of 9-methylfluorenyl in THF at ambient temperatures produced PMMA (MWD = 2.16) in low yield (24%).[13] In agreement with this, we found that the anionic polymerization of MMA in the presence of the tetrabutylammonium cation (n-Bu_4N^+) in THF at ambient temperatures using triphenylmethyl (Ph_3C^-) as the initiator produced high molecular weight PMMA (M_n = 322 500) in low yield (5%) and low initiator efficiency (<1%).[14] The low polymerization yield and low initiator efficiency may be attributed to the Hoffman elimination reaction of the Ph_3C anion or of the propagating enolate with n-Bu_4N^+. Other n-Bu_4N^+ carbanions with lower basicities (e.g. 9-ethylfluorenyl) were explored as initiators, in order to prevent the Hoffman elimination reaction, but initiation rates were slow, resulting in wider MWDs.[14] The use of Ph_4P^+ cations in phase-transfer reactions prompted us to explore the use of Ph_4P^+ salts of carbanions as initiators for the polymerization of MMA.[15]

The triphenylmethyl carbanion tetraphenylphosphonium salt ($Ph_3C^-Ph_4P^+$), is formed by cation exchange at −78 °C of (triphenylmethyl)potassium ($Ph_3C^-K^+$) and tetraphenylphosphonium chloride ($Ph_4P^+Cl^-$) in THF (Scheme 1). The potassium chloride (KCl) formed can be filtered off, but this is not necessary for the subsequent polymerization. The cation exchange proceeds very rapidly (seconds) and quantitatively even at −78 °C,[15] and it is characterized by a change in the red color of the $Ph_3C^-K^+$ salt solution (λ_{max} = 492 nm) into a deep maroon color of the phosphonium salt solution (λ_{max} = 506 nm).[16] The shape and the extinction coefficient of the absorption band remained the same, indicating that the structure of the carbanion is unchanged.

Scheme 1. Proposed Mechanism for the Anionic Polymerization of MMA in the Presence of Ph_4P^+ in THF at Ambient Temperatures

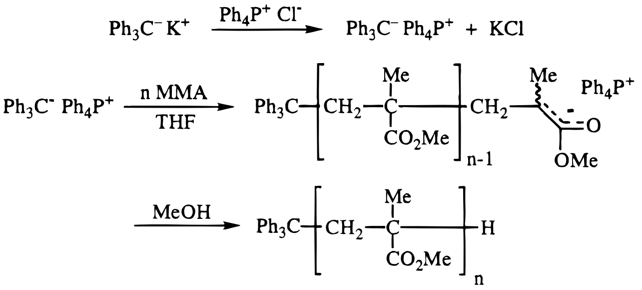

Table 1. Anionic Polymerization of MMA Initiated by $Ph_3C^-Ph_4P^+$ in THF

T (°C)	M_n[a]	MWD[e]	% yield	f[b]	mm[c]	mr[c]	rr[c]
0	8 500 (9 300)[d]	1.12	>95	0.46	0.09	0.37	0.54
0	8 600	1.13	>95	0.54			
0	26 400	1.10	87	0.40			
0	28 900	1.04	91	0.32	0.07	0.38	0.55
0	29 100	1.17	>95	0.36	0.07	0.42	0.51
20	13 200	1.20	>95	0.39			
20	13 200	1.18	>95	0.68			

[a] Calibration with PMMA standards. [b] Initiator efficiency (f) = $M_{n(calc)}/M_{n(SEC)}$. [c] By ^1H NMR (360.13 MHz) integration of α-methyl resonances. [d] Determined by ^1H NMR integration of Ph_3C^- against the CH_2 groups of the chain. [e] MWD after precipitation of the polymer in hexane.

The polymerization is carried out by dropwise addition of a solution of MMA (10 mL of 1.0 M MMA in THF) to a 50 mL solution of $Ph_3C^-Ph_4P^+$ in THF (~2×10^{-3} M) (Scheme 1). The rate of initiation is very rapid, as observed by an instantaneous change in color from deep maroon to orange-red. The rate of polymerization is very rapid, the polymerization being complete in a matter of seconds.[17] Termination of the polymerization with methanol is rapid, as indicated by an instantaneous disappearance of the orange-red color.[18]

Table 1 summarizes some of the results obtained for the polymerization of MMA at 0 and 20 °C in THF. The polymers produced generally have a narrow MWD (1.04−1.20) especially at 0 °C and are obtained in quantitative yields, indicating that the polymerization is living and proceeds with little chain termination even at ambient temperatures. The intramolecular Claisen type termination reaction, which is usually observed in the anionic polymerization of MMA at higher temperatures (T > −20 °C) in the presence of alkali cations is greatly reduced in this polymerization system, as seen from the relatively narrow MWD of the polymers. The M_n determined by ^1H NMR integration of the aromatic versus the CH_2 resonances of the chain is generally in good agreement with the SEC values.[18]

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The large size of the Ph_4P^+ cation (r = 5.7 Å)[19] probably facilitates the formation of narrow MWD PMMA at ambient temperatures by reducing the rate of the above side reactions.[20,21] The initiator efficiency, f, defined as $M_{n(calc)}/M_{n(exp)}$ is found to be between 30 and 70% on the basis of the original $Ph_3C^-K^+$ concentration prior to cation exchange (Table 1). The less than quantitative apparent initiator efficiencies observed are only apparent and are due to the presence of some water in the Ph_4PCl and to some initiator decomposition prior to polymerization. The reaction between the Ph_3C^- and the Ph_4P^+ cation is suppressed (as compared to that with n-Bu_4N^+), consistent with the absence of highly reactive alkyl β-hydrogens. This was confirmed by the greater stability of $Ph_3C^-Ph_4P^+$ compared to the corresponding n-Bu_4N^+ salt that decomposes in a few (~10) seconds at ~22 °C. The decomposition of $Ph_3C^-Ph_4P^+$ was monitored *via* UV−vis spectroscopy at ambient temperature and shows a first-order decomposition ($t_{1/2}$ = ~200 s). Thus the efficiency of the initiator depends upon experimental conditions, especially the storage time and temperature of the $Ph_3C^-Ph_4P^+$. Control of molecular weight is possible provided that the polymerization is performed immediately after the formation of $Ph_3C^-Ph_4P^+$. The stereochemistry of the PMMA produced in the presence of Ph_4P^+ (~50% *rr*, Table 1)[17] is similar to that obtained by GTP[1,22] and other MMA polymerizations[9] at comparable temperatures. Polymerization kinetics carried out elsewhere show first-order kinetics in monomer and a linear relation between conversion and number average molecular weight.[23] Preliminary experiments have indicated that this method is applicable to other acrylate monomers such as n-butyl acrylate and to 2-vinylpyridine and to the synthesis of block copolymers at ambient temperatures.[14]

In conclusion, the anionic polymerization of MMA in the presence of Ph_4P^+ at ambient temperatures is capable of producing narrow MWD PMMA with a reasonable degree of control. This new polymerization method has potential for the synthesis of PMMA, other polyacrylates, and their block copolymers at ambient temperatures.

Acknowledgment. We would like to thank the National Science Foundation-DMR (Polymers Program) for support of this research.

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(17) Preliminary results determined by A. H. E. Müller et al. (private communication) using a flow tube reactor show that the rate of polymerization is very rapid since the polymerization is complete in less than 2 s at 0 °C (and less than 1 s at 20 °C).

(18) The orange red color has now been shown to be due to the formation of a phosphor ylide formed by addition of the enolate anion to one of the phenyl rings of the PPh_4^+ ion (Baskaran, D.; Zagala, A.; Mueller, A. H. E.; Hogen-Esch, T.E. To be published).

(19) The ^1H NMR analyses were performed using a Bruker AM-250 MHz FT-NMR, and the concentrations of the PMMA solutions used in the experiments were 10−15 wt % in $CDCl_3$. The stereochemistry of the polymers was determined through integration of the ^1H NMR resonance absorptions of the methyl groups.

(20) AM1 (Austin Model) semi-empirical calculations (Spartan Program).

(21) Reetz et al.[5] postulated that the intramolecular Claisen type termination reaction is decreased in the anionic polymerization of n-butyl acrylate at ambient temperatures because the tetrabutylammonium alkoxide formed is thermodynamically and kinetically unfavorable due to the weak electrostatic interaction between the n-butoxide and the bulky n-Bu_4N^+ cation.[3]

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MA951405K