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Novel Carbanionic Polymerization of Methyl Methacrylate by Unusual Electron-Transfer Catalysis

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ABSTRACT: Supramolecular complexes of alkali metals and their capability of electron transfer and generation of carbanions have been utilized in the polymerization of methyl methacrylate. Unusual living, metal-free polymers of methyl methacrylate, their structure, and properties are discussed. The structure of polymers and polymerization mechanism were analyzed by ^{1}H, ^{13}C, ^{39}K, and ^{13}C DEPT (distortionless enhancement by polarization transfer) NMR spectroscopy.

Introduction

Poly(methyl methacrylate) (PMMA) and its copolymers have found a great range of applications because of their biocompatibility, as well as good mechanical and thermomechanical properties,[1-4] excellent weatherability, and unique transparency. Until the beginning of the 1980s, the free radical polymerization of MMA was the only commercial method of making PMMA. However, radical polymerization cannot provide the proper control of the polymerization process. The traditional anionic polymerization of MMA yielding polymers with well-defined structures can be performed under carefully controlled conditions, and only at low temperature (−75 °C), to avoid side and termination reactions.[5] The progress in living anionic polymerization of methyl methacrylate has recently been achieved by proper selection of solvent, temperature, and initiators.[6-8] Although several initiator systems—alkyllithium,[9] Al(C_2H_5)$_3$·TiCl$_4$,[10] Grignard reagents, e.g., *i*BuMgBr or (*m*-vinylbenzyl)MgEt,[11] are known to produce syndiotactic PMMA, the molecular weights are small and the polydispersities rather broad (1.2−1.8). On the other hand, the group-transfer polymerization process (GTP)[12,13] needs rigorous monomer and solvent purification to remove protic impurities. Further investigations led to new polymerization techniques of MMA such as catalytic chain-transfer polymerization,[14] atom-transfer radical polymerization,[15] and metal-free anionic polymerization.[16] Organolanthanide(III) complexes[17] have been also proposed as effective initiators for MMA polymerization.

The anionic polymerization of methyl methacrylate initiated by alkali metal complexes with arenes was mentioned first by Szwarc.[18] The discovery of crown ethers by Pedersen[19] and cryptands by Lehn[20] capable of complexing alkali metal cations provided new opportunities in organic synthesis.[21] The solubility of alkali metals in aprotic solvents has been demonstrated in the presence of these macrocyclic ligands.[22] These so-called “alkali metal organic solutions”, containing solvated electrons, metal anions, and complexed cations, have been used as initiators for polymerization.[23-26] However, the composition of such solutions was not precisely defined, and polymerization results were not well reproducible. The kinetic studies of metal dissolution enable preparation of well-defined metal solutions containing alkali metal ion pairs and only negligible concentration of electrons.[27,28]

In this paper we present an unusual polymerization of methyl methacrylate, initiated by a well-defined supramolecular complex of potassium or sodium−potassium alloy with 18-crown-6 in tetrahydrofuran. The ability of alkali metal complexes solubilized in an etheral solvent to act as efficient anionic initiator in the reaction with methyl methacrylate and preparation of well-defined “living” polymers is demonstrated.

Experimental Section

Materials. Methyl methacrylate (from Fluka) was purified as described in ref 25. Before polymerization the monomer was redistilled under reduced pressure, and the fraction boiling at 39 °C (70 mmHg) was collected. 18-Crown-6 was purified as described previously.[27]

THF was purified as described in ref 29 and then distilled over a sodium−potassium alloy in an atmosphere of dry argon.

Preparation of the Initiator. The 0.03 mol/L THF solution of the supramolecular complex of potassium was obtained

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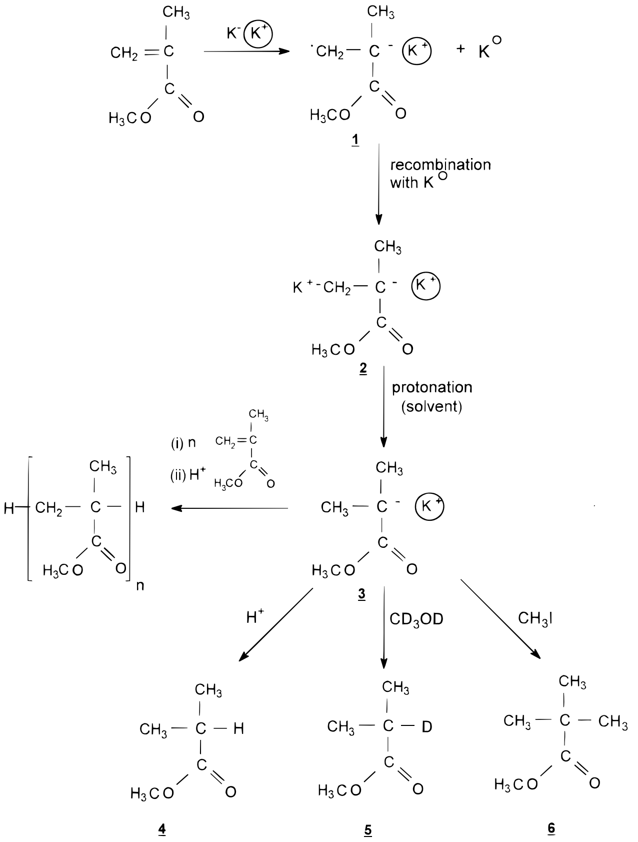
Table 1. Homopolymerization of MMA Initiated by Na^-/K^+,18C6 or K^-/K^+,18C6 Complex at 20 °C

							microstructure (triads)		
alkali metals[a]	I_0 [mol/L]	m_0 [mol/L]	$10^{-3}M_n$ (exp)[b]	$10^{-3}M_n$ (calc)[c]	M_w/M_n	T_g [°C]	mm	mr	rr
Na/K (1:3)	0.0118	1.102	10.1	9.4	1.2	112	0.07	0.37	0.56
Na/K (1:3)	0.0059	2.482	41.8	42.1	1.3	117	0.08	0.37	0.55
Na/K (1:3)	0.0017	1.560	95.9	93.6	1.5	119	0.09	0.36	0.55
Na/K (1:3)	0.0013	1.872	146.0	144.0	1.6	120	0.08	0.39	0.53
Na/K (1:3)	0.0013	2.925	215.0	225.0	1.6	124	0.08	0.35	0.57
K	0.0210	1.176	5.7	5.6	1.3	111	0.06	0.37	0.57
K	0.0110	1.518	14.0	13.8	1.3	112	0.07	0.36	0.57
K	0.0072	1.663	22.1	23.1	1.4	112	0.05	0.35	0.60
K	0.0033	2.600	75.5	78.7	1.5	118	0.08	0.36	0.56

[a] Alkali metal complexes obtained from Na/K alloy or from K mirror by dissolution in THF containing 18-crown-6. Metal complexes form in solution ion pairs, e.g., K^+crown,K^- or K^+crown,Na^- respectively. Preparation of initiators is described in the Experimental Section. [b] Estimated by GPC using PMMA standards with narrow molecular weight distribution. [c] Calculated from $(m_0/I_0)M$ (where m_0 and I_0 are the initial concentration of monomer and initiator, respectively; M is the molecular weight of the monomer).

Scheme 1



by the contact of the potassium mirror with a solution of 18-crown-6 in THF (0.03 mol/L) for 15 min at the temperature 20 °C under an argon atmosphere. The dissolved potassium complex consists of potassium ion pairs: K^+crown,K^-. In some experiments, the 0.03 mol/L THF solution of the supramolecular complex of sodium−potassium alloy was obtained by the contact of the alloy (3:1 weight ratio of potassium to sodium) with a solution of 18-crown-6 in THF (0.03 mol/L) at a temperature of 20 °C. The dissolved sodium−potassium complex consists of potassium K^+crown,Na^- ion pairs. After 15 min the resulting blue mixture was filtered through a coarse frit to the thermostated glass reactor.

Model Reactions of Methyl Methacrylate with Supramolecular Complexes of Potassium. The THF solution of 18C6 (0.2 mol/dm^3) was kept in contact with a potassium mirror for 15 min at 0 °C under an inert gas atmosphere. Then, to the blue metal solution, filtered through glass frit, was added the equivalent amount of methyl methacrylate in THF solution until the blue color of the solution disappeared. After 10 min of stirring of the reaction mixture protonation, methylation, or deuteration was performed by addition of methanol, iodomethane, or methyl-d_3 alcohol-d_1 in THF, respectively. Discolorized solution was analyzed by GC-MS. The following product was obtained:

Protonation of Reaction Mixture: 2-methylpropanoic acid methyl ester. GC-MS *m/e* (intensity): 103 (M^+ + 1, 1), 102 (M^+, 20), 87 (52), 71 (82), 59 (53), 43 (43).

Deuteration of Reaction Mixture: deuterated 2-methylpropanoic acid methyl ester (2-methylpropanoic acid methyl ester-α*d*). GC-MS, *m/e* (intensity): 104 (M^+ + 1, 1), 103 (M^+, 20), 88 (50), 72 (50), 60 (21), 59 (21), 44 (40), 43 (43).

Methylation of Reaction Mixture: 2,2-dimethylpropanoic acid methyl ester. GC-MS, *m/e* (intensity): 116 (M^+, 4), 101 (3), 85 (6), 73 (5), 59 (6), 57 (100), 41 (47).

The identity of products of the reaction mixture has been confirmed by their MS data compared with those reported for the respective pure chemicals (NIST and John Wiley & Sons, Inc., mass spectral libraries).

Polymerization. The polymerization was conducted in THF at 20 °C. The solution of an initiator was introduced into the thermostated glass reaction chamber, and next the solution of MMA in THF was slowly added. The concentrations of monomer and initiator are provided in the Table 1. The polymerization was terminated by adding methanol. After completion of polymerization (5 min) the polymer was precipitated in hexane. The precipitate was washed with hexane several times and dried under vacuum. The results are presented in Table 1.

Measurements. The structure and tacticity of polymers were analyzed by ^{1}H, ^{13}C, and ^{13}C DEPT[30] (distortionless enhancement by polarization transfer) NMR spectroscopy, using a Varian VXR-300 multinuclear spectrometer. Number-average molecular weights were determined by the VPO technique in $CHCl_3$ using a Knauer vapor pressure osmometer and by GPC. The molecular weight distribution of the obtained polymer was determined by GPC according to poly(methyl methacrylate) standards with low polydispersity (PL Lab.). GPC experiments were conducted in THF at 35 °C, using the Spectra-Physics 8800 gel permeation chromatograph.

The glass transition temperature (T_g) of polymer samples was determined by differential scanning calorimetry (DSC) on a Du Pont 9000 instrument, calibrated with indium and gallium. Samples were heated at 170 °C and cooled to 20 °C and scanned repeatedly at rate of heating 20 °C/min.

Results and Discussion

The mechanism of the reaction of methyl methacrylate (MMA) with a supramolecular complex of potassium (or sodium−potassium alloy) was studied. It turned out that in the reaction of methyl methacrylate with the alkali metal complex two electrons are transferred from the initiator to the MMA monomer to form a dianion, which instantly undergoes protonation by the solvent and yields a respective carbanion which is capable of inducing polymerization reaction. The main products in the model reaction of MMA with the complex of potassium, molar ratio 1:1, after protonation by CH_3OH, deuteration by CD_3OD, or methylation by CH_3I are 2-methylpropanoic acid methyl ester **4** or the respective

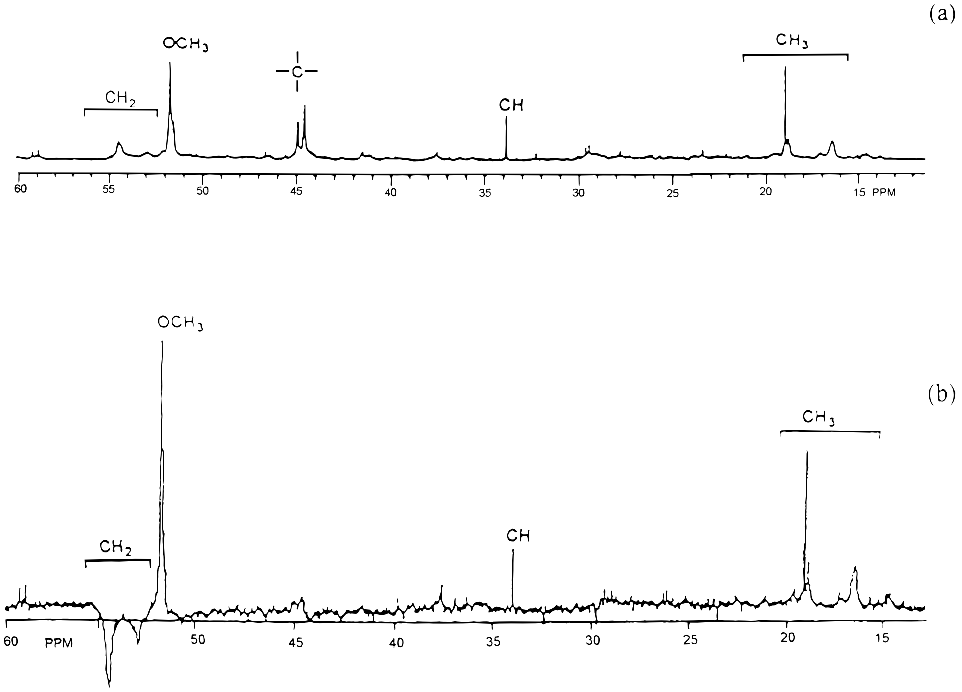


Figure 1. ^{13}C NMR (a) and ^{13}C DEPT (b) spectra of the PMMA oligomer aliphatic region obtained in the presence of the K^-/K^+,18C6 complex in THF, at 20 °C (MMA:K^- = 2:1).

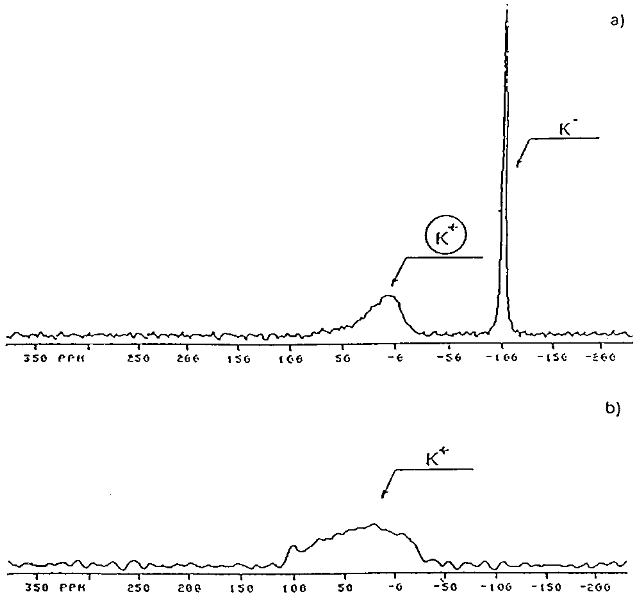


Figure 2. ^{39}K NMR spectrum of the potassium complex with 18C6 (a) before the reaction with methyl methacrylate and (b) after the reaction.

deuterated compound **5** as evidenced by GC-MS analysis. The methylation of 1:1 reaction products by CH_3I yields 2,2-dimethylpropanoic acid methyl ester **6** (Scheme 1).

The mechanism of polymerization if a monomer is in excess was provided by NMR spectrometry of obtained oligomers (Scheme 1).

The ^{13}C NMR and the ^{13}C DEPT (distortionless enhancement by polarization transfer) spectra of oligomers (Figure 1), obtained in the reaction of MMA with K^-/K^+,18C6 complex in THF (MMA:metal complex = 2÷5:1), indicates the presence of a terminal methine proton, which is formed as the end group by two electrons transfer to the monomer MMA.

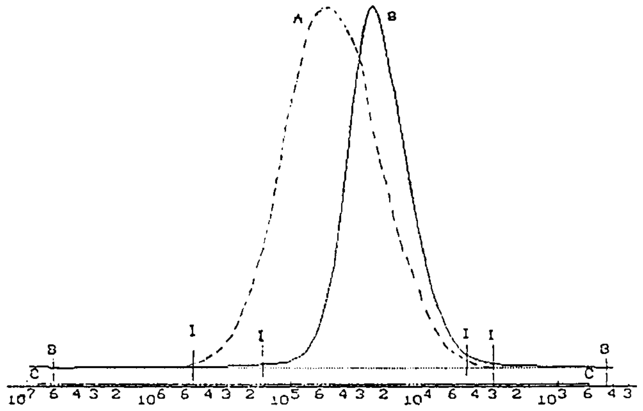


Figure 3. GPC curves of PMMA samples prepared with supramolecular complex of sodium−potassium in THF at 20 °C. (A) M_n = 146 000, (B) M_n = 10 100.

Another evidence of transfer of two electrons from the initiator toward monomer at the initiation step was provided by ^{39}K NMR. It was found that the signal of the potassium anion in the ^{39}K NMR spectrum of the metal complex disappeared after the reaction with methyl methacrylate, the resonance signal of the cation becoming more intensive (Figure 2). One explanation is that in this reaction the potassium anion, after the transfer of two electrons to the methyl methacrylate molecule, is converted into the potassium cation.

On the basis of experimental data, the following course of this reaction can be proposed (Scheme 1). In the reaction of the supramolecular metal complex with MMA, after the transfer of one electron, radical anion **1** is formed. Next, the recombination of this radical anion **1** with potassium (K^0) yields MMA dianion **2**. Due to instant protonation by THF solvent, a carbanion **3** is formed. After protonation, deuteration, or methylation, 2-methylpropanoic acid methyl ester, deuterated 2-methylpropanoic acid methyl ester, or 2,2-dimethylpropanoic acid methyl ester is formed, respectively. If a

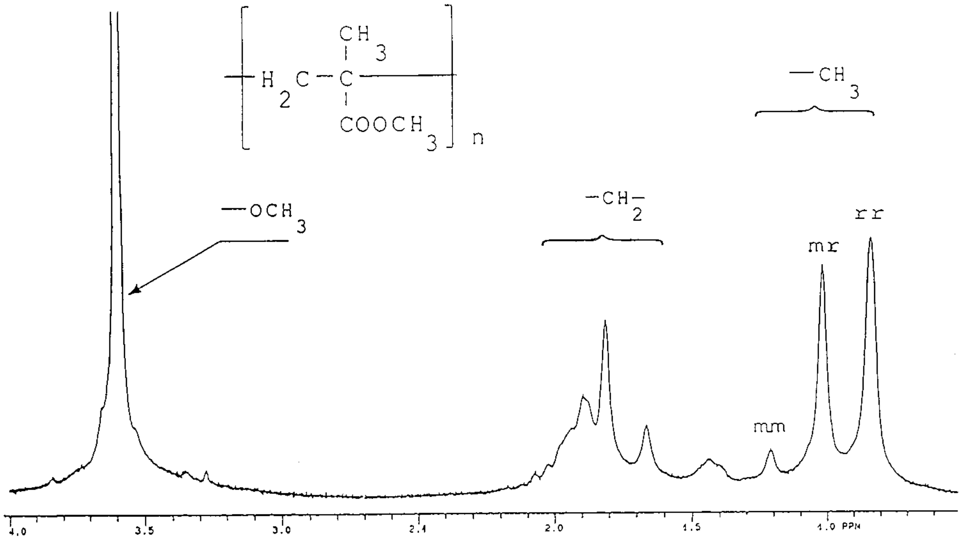


Figure 4. ^{1}H NMR (300 MHz) spectrum of PMMA polymer obtained in the presence of supramolecular complex of sodium–potassium alloy in THF, at 20 °C.

methyl methacrylate is present in an excess, in the reaction medium poly(methyl methacrylate) possessing methine proton end group is formed as confirmed by ^{13}C NMR and ^{13}C DEPT experiments (Figure 1).

The results of MMA polymerization initiated with Na^-/K^+,18C6 or K^-/K^+,18C6 complexes in THF at temperature 20 °C are shown in Table 1. It was found that the anionic polymerization of MMA initiated by supramolecular complexes of sodium–potassium alloy or potassium in THF proceeds at room temperatures were fast and polymers obtained exhibit high molecular weights over 200 000 M_n (Table 1). To demonstrate the living character of this process, polymerization of MMA in THF at 20 °C has been carried out using various monomer/initiator molar ratios. A linear dependence of experimental molecular weights and calculated ones is observed for a broad molecular weight range. Thus, the molecular weight of polymers could be controlled by changing the ratio of initial concentrations of the monomer and the initiator as shown in Table 1. The number-average molecular weight of the polymer agreed well with the expected value. In most cases high conversions up to 100% and M_w/M_n of 1.2–1.3 were observed.

Only for very high molecular weight polymers (over 140 000 M_n) was the M_w/M_n higher than 1.6. This effect is probably due to the increased temperature and the high exothermic effect in very viscose medium of the reaction. The formation of block copolymers of MMA with ϵ-caprolactone and δ-valerolactone indicating the "living" type of the reaction will be published in a separate paper.[31]

The homopolymerization of MMA with a supramolecular complex of sodium–potassium or potassium as initiator yields polymers showing the unimodal MWD (Figure 3). All obtained PMMA samples were amorphous (Table 1).

The analysis of α-methyl region of the PMMA ^{1}H NMR spectra[32] (Figure 4) indicates that the polymerization leads to heterotactic polymers rich in syndiotactic triads (Table 1).

Conclusions

The anionic polymerization of MMA, in the presence of a novel initiator–supramolecular complex of potassium or sodium–potassium alloy with 18-crown-6 in THF, yields PMMA polymers. The described supramolecular catalyst is extremely convenient because it works perfectly at room temperature, yielding polymers with molecular weights over 200 000 M_n and with low polydispersity (1.2–1.6). The living character of the polymerization provides opportunities for tailored PMMA synthesis and copolymer synthesis. The unusual mechanism of this novel polymerization was demonstrated.

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