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Anionic Polymerization in Oxiranes. Polymerization of Methyl Methacrylate and 2-Vinylpyridine in Ethylene Oxide†

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ABSTRACT: The anionic polymerization and copolymerization of methyl methacrylate (MMA), 2-vinylpyridine (2-VP), and ethylene oxide (EO) in an EO medium was studied in the temperature range between −70 and +20 °C. Organolithium (α-lithioethyl isobutyrate and oligostyryllithium) and organopotassium (t-BuOK and cumylpotassium) initiators were used. It was found that at temperatures below −20 °C the anionic homopolymerization of MMA initiated by t-BuOK proceeds at an extremely low rate. The polymers were predominantly hetero- and syndiotactic with a comparatively broad molecular mass distribution (M_w/M_n = 1.5–11.0). At temperatures higher than 0 °C the active centers of PMMA and P(2-VP) initiated the polymerization of EO. Block copolymers and insoluble gels (in the case of MMA) with PEO segments were obtained.

Introduction

Cyclic ethers are the most common solvents used in the anionic polymerization. The widespread use of the ethers as reaction media seems to be due to the moderate dielectric constants in addition to their donor character. Being effective electron pair donors, cyclic ether molecules participate in the counterion solvation of the growing polymer chain, thus influencing the mode of monomer addition.

The small molecule of EO occupies the solvation shell of the cation without any steric hindrance. This is the most reasonable explanation for the higher solvating power of EO and propylene oxide toward alkali-metal salts in comparison with tetrahydrofuran (THF) or tetrahydropyran (THP)[1-4] contrary to the well-documented basicity sequence of cyclic oxides.

In contrast to the five- and six-membered ethereal rings, three-membered cycles are not known as reaction media in anionic polymerization. They could be easily involved in ring-opening addition reactions leading to polymer formation. The driving force for a ring-opening reaction is the relief of the strain energy of the EO ring. Ring opening requires a significant loss of energy;[5] thus, polymerization could be avoided by keeping the reaction mixture at temperatures below 0 °C.

The interest in the use of EO or other oxiranes as a medium in anionic polymerization processes results not only from its good solvating properties but also from its relatively high dielectric constant (13.9 at −1 °C), an important factor for the rates of solvent-dependent reactions. Moreover, a suitable change in the polymerization temperature could lead to the anionic polymerization of solvent molecules, resulting in formation of block or multiblock copolymers.[6]

The monomers MMA and 2-VP were used in the present investigation for several reasons. The anionic polymerization of both monomers has been thoroughly studied. The tacticity of PMMA strongly depends on the solvating power of the medium, contrary to that of P(2-VP). Their copolymers with EO are materials with interesting amphiphilic properties.

Experimental Part

A high-vacuum-line technique (10^{-6} mbar) was used for all procedures and syntheses. Monomers (MMA and 2-VP) and solvents (EO, THF, and toluene) were dried over CaH_2. After degassing and distilling in vacuo, the monomers were distributed into ampules provided with break-seals.

α-Lithioethyl isobutyrate (α-LiEtIB) and potassium *tert*-butoxide (t-BuOK) were synthesized according to Lochmann et al.[7,8]

The polymerization was carried out in reaction vessels shown in Figure 1. The solutions of monomer and initiator in EO were mixed after cooling under vigorous stirring. Polymerization was stopped by addition of hydrochloric acid. The polymers were precipitated in petroleum ether.

Block copolymers were synthesized by increasing the polymerization temperature up to 20 °C. In the case of MMA, the

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† Dedicated to Prof. Dr. J. Smid on the occasion of his 60th birthday.

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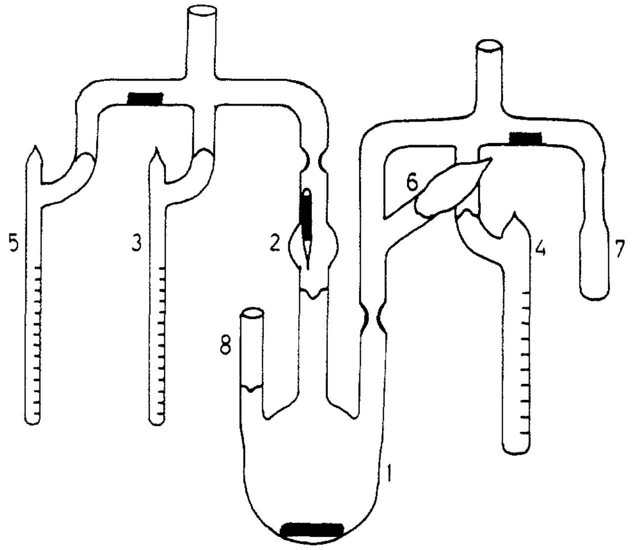


Figure 1. Apparatus for anionic polymerization of MMA in EO: (1) reaction vessel, (2) monomer solution in EO, (3, 4) ampules with EO, (5) ampule with MMA, (6) initiator in toluene, (7) vessel for collecting the toluene from the initiator solution in 1, (8) break-seal. 1 and 2 are immersed in a cryostat.

Table I
Anionic Polymerization of MMA in EO (Initiator, α-LiEtIB; Reaction Time, 60 min)

no.	T, °C	[M], mol/L	[In] × 10^3, mol/L	yield, %	M_n	M_w/M_n	efficiency
1	−20	1.87	5.2	70	66 500	2.2	0.38
2	−40	1.92	5.1	100	76 000	1.8	0.50
3	−40	1.84	9.2	99	24 000	1.7	0.84
4	−60	1.70	4.8	99	58 000	2.2	0.61
5	−60[a]	1.90	4.7	100	101 000	1.4	0.41

[a] In the presence of LiCl, [LiCl]/[In] = 3.

product was extracted with methanol and benzene; thus, soluble block copolymers were separated from the insoluble gel obtained.

Molecular masses and molecular mass distribution (MWD) were determined by GPC analysis in THF on a Waters apparatus. The columns (10^3, 10^4, 10^5, and 10^6-Å Waters and Shodex 802) were calibrated with PMMA standards; the flow rate was 1.5 mL/min. The analysis was performed also on a high-performance column for the exclusion chromatography of polymers (Lenchrom, USSR), allowing more precise determination of the MWD in the range 2×10^3–2×10^6; the flow rate in this case was 0.3 mL/min.

IR spectra were recorded on a M-80 spectrometer (Carl-Zeiss), Jena as films (for soluble block copolymers) and as swollen in $CHCl_3$ gels (for insoluble fractions).

^1H NMR and ^{13}C NMR spectra were recorded in $CHCl_3$ on a Brucker WM 250 spectrometer. Calorimetric measurements were performed on a DSC 7 apparatus (Perkin-Elmer); the heating rate was 10 °C/min.

Results and Discussion

I. Polymerization of MMA Initiated by α-LiEtIB. α-LiEtIB resembles a model of the one-unit active center (AC) in the anionic polymerization of MMA. The use of this initiator avoids side reactions with the ester function of the monomer.[8,9]

α-LiEtIB is able to react not only with MMA but also with EO. Homopolymerization of EO is not possible because lithium alkoxide does not promote the polymerization of EO.[10] The competition between both reactions becomes clear by polymerization temperatures higher than −40 °C, where polymer yield never exceeds 100% (Table I). Obviously, during the polymerization part of the AC turns into unreactive alkoxide, which forms mixed associates with the PMMA AC. AC/alkoxide aggregates produce polymers with comparatively broad MWD. The relative breadth of the distribution decreases upon addition of the μ-type ligand LiCl. (According to Jerome et al.[11] LiCl is very effective in avoiding side reactions and destroying AC aggregates in anionic polymerization of methacrylates, thus influencing the MWD).

Table II
Triad Tacticity of PMMA, Obtained by Anionic Polymerization in Different Solvents with Organolithium Initiators

solvent	polymn temp, °C	tacticity, % mm	mr	rr	ref
DME	−57	1	16	83	12
THF	−45	1	22	77	12
EO	−20	5	28	67	a
EO	−40	4	29	67	a
EO	−60	3	22	75	a
EO	−60	2	22	76	b
THP	−35	6	32	62	13
DO	13	10	35	55	13
toluene[c]	−78	70	20	9	14
toluene[d]	−78	93	5	1	14
toluene + {2,2,1}	−40	5	34	62	15

[a] This work. [b] In the presence of LiCl, [LiCl]/[In] = 3. [c] $[M]_0$ = 4.75 mol/L. [d] $[M]_0$ = 0.04 mol/L.

It is assumed that the tacticity depends mainly on the competition between the solvent and the monomer for coordination sites of the counterion. According to our previous results on binding of lithium picrate to different types of monomers and solvents,[4,16] lithium cations are more easily captured by propylene oxide molecules (analogy with EO) than by MMA. As shown in Table II, PMMA obtained in an EO medium is predominantly syndiotactic with a comparatively high heterotactic content. The triad tacticity is close to that in THF. Addition of LiCl does not influence the polymer structure.

II. Polymerization of MMA, Initiated by t-BuOK. It is well-known that t-BuOK is not an effective initiator for anionic polymerization since most of the alkoxide is present as aggregated species. For example, the alkoxide associates appreciably evenly in hexamethylphosphoramide.[17] In the case of reactions of alkoxides with MMA[18] and EO,[17] the active species are usually considered to be monomeric. However, the sensitivity of the initiator solutions on different types of association–dissociation equilibria makes it suitable to study the dependence between the initiator efficiency and media solvating power. The degree of association of t-BuOK must barely decrease in EO, although its strong solvating properties promote dissociation of the aggregates and enhance the reactivity of the alkoxide.

The data in Table III show that the anionic polymerization of MMA seems to be associated with different types of reactions involving aggregation–disaggregation equilibrium of AC, termination, and chain-transfer reactions.

A serious disadvantage of the process is the observed fairly broad MWD's if compared with those of polymers prepared by "ideal" living anionic polymerization, as well as PMMA obtained from α-LiEtIB (Table I).

This undesired effect can be explained by three factors: (1) slow initiation; (2) propagation on mixed associates (several types of AC) with different reactivity and slow dynamics of equilibrium; (3) transesterification reactions between an oxirane AC and the methoxy group in MMA units.

According to Gold's treatment,[19] for a "living" polymerization on one type of active species, M_w/M_n never exceeds 1.375, even at a very high k_p/k_i ratio ($k_p/k_i = 10^6$). Obviously, slow initiation cannot be the only explanation for the broad MWD.

Table III
Polymerization of MMA in EO, Initiated by t-BuOK

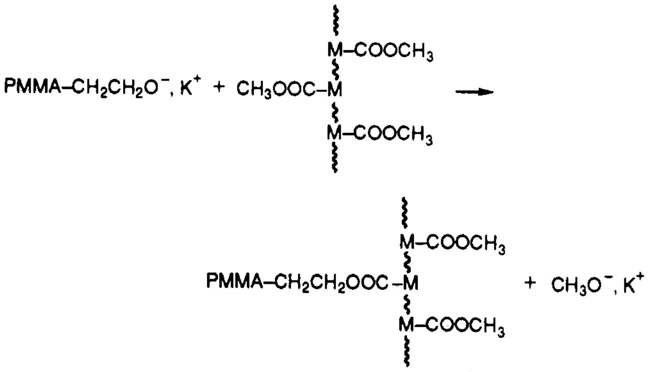
no.	T, °C	time, min	$[M]_0$, mol/L	$[I] \times 10^3$, mol/L	yield, %	$\bar{M}_n$	M_w/M_n	efficiency	$k_{app} \times 10^2$,[a] $L \cdot mol^{-1} \cdot s^{-1}$
6	-55	60	0.51	5.00	100	14 500	3.0	0.70	
7	-55	10	0.91	4.70	6	4 000	5.5	0.29	7.6
8	-55	25	0.94	4.70	17	5 800	4.2	0.59	4.5
9	-55	30	0.99	4.90	22	7 000	4.0	0.63	4.4
10	-55	40	1.00	5.00	30	9 000	3.6	0.67	4.5
11	-55	60	0.92	5.40	100	20 500	3.1	0.83	
12	-55	120	0.94	5.45	100	19 000	6.2	0.91	
13	-55	10	1.91	4.95	12	4 300	4.1	0.96	4.5
14	-55	20	1.91	4.95	20	15 000	3.2	0.51	7.3
15	-55	25	1.82	4.75	86	41 000	6.5	0.80	
16	-55	30	1.88	4.80	96	62 000	11.3	0.61	
17	-55	5	2.75	4.70	10	17 500	2.7	0.33	22.3
18	-55	15	2.59	4.50	42	24 000	10.1	1.00	
19	-55	25	2.54	4.10	100	96 000	9.3	0.64	
20	-55	40	2.68	5.00	100	51 000	11.6	1.05	
21	-30	5	1.92	4.75	88	52 000	11.2	0.68	
22	-30	30	1.99	4.70	83	50 000	8.1	0.70	
23	0	10	1.79	4.35	87	18 500	6.5	1.94	
24[b]	-70	2	0.42	5.00	6	9 000	1.5	0.06	184
25[b]	-70	5	0.44	5.00	11	14 000	1.5	0.07	112
26[b]	-70	30	0.53	5.1	91	24 000	2.2	0.39	

[a] The concentration of active sites C^* is determined by the yield of the precipitated polymer x_p and its degree of polymerization $\bar{P}_n$: $c^* = [M]_b x_p/\bar{P}_n$; k_{app} is calculated by $\ln [M]_0/[M]_t] = k_{app}C^*t$. [b] Initiator, cumylpotassium.

Even at low temperatures the solvent is not fully inert; thus, the addition of epoxide to the methacrylate growing center may occur:

$$\sim\!\!\sim MMA^-,K^+ + EO \rightarrow \sim\!\!\sim MMA\text{–}CH_2CH_2O^-,K^+$$

Less reactive potassium alkoxide could be formed which is also capable of initiating the anionic polymerization of MMA and participating in transesterification reactions.[6] If the latter reactions proceed, they would lead to the formation of branched structures:



$$PMMA\text{–}CH_2CH_2O^-,K^+ + CH_3OOC\text{–}\underset{\substack{\wr\\ M\text{–}COOCH_3\\ \wr}}{\overset{\substack{\wr\\ M\text{–}COOCH_3\\ \wr}}{M}} \longrightarrow PMMA\text{–}CH_2CH_2OOC\text{–}\underset{\substack{\wr\\ M\text{–}COOCH_3\\ \wr}}{\overset{\substack{\wr\\ M\text{–}COOCH_3\\ \wr}}{M}} + CH_3O^-,K^+$$

Accordingly, chain transfer is possible since potassium methoxide initiates the polymerization of MMA and EO. Usually the average degree of branching increases with conversion, which gives rise to the broadening of MWD. When $[M]_0 = 1$ mol/L, results are quite opposite (Table III) which is evidence of the low rate of the transesterification reaction in comparison with chain propagation under experimental conditions for the first set of experiments (nos. 6–11, Table III). However, when terminating the reaction after 120 min, the MWD doubled. Obviously, after the course of polymerization intermolecular reactions (branching after transesterification) occur, leading to broadening of the distribution.

In the presence of unreacted t-BuOK, formation of adducts with the propagating $PMMA^-,K^+$ sites, parallel with the self-association of AC, is very plausible. As the polymerization proceeds, the concentration of aggregated species will gradually decrease with conversion, due to the continued initiation and the equilibrium shift in favor of the unassociated AC. The overall result would be a tendency to narrow the initially broad MWD.

Table IV
Dependence of the Efficiency of t-BuOK on the Solvent Nature and Additive (polymerization Temperature, -60 °C)[a]

			toluene		
	toluene	THF	crown-6	{2,2,2}	EO
efficiency	0.003	0.043	0.21[b]	0.67[b]	0.7[c]

[a] $[MMA]_0 = 0.5$ mol/L; $[In]_0 = 0.005$ mol/L. [b] Crown-6–dicyclohexyl-18-crown-6.[15] [c] Experiment no. 6, Table III.

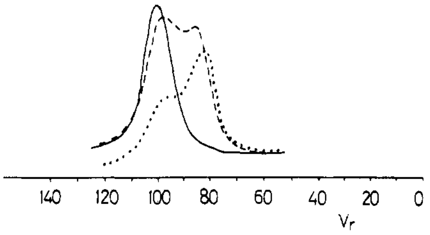


Figure 2. Molecular mass characteristics of PMMA obtained at different degrees of conversion: (—) 10% conversion (expt no. 17, Table III); (- - -) 42% conversion (expt no. 18, Table III); (· · ·) 100% conversion (expt no. 20, Table III).

Data presented in Table IV show that in case of low initial monomer concentration the efficiency of t-BuOK in EO is comparable to that of the complex t-BuOK–{2,2,2} in toluene.

Since the carbanion of cumylpotassium reacts with EO by several orders more quickly than the potassium alkoxide,[20,21] its initiator efficiency in MMA polymerization is poor. Obviously, the narrower MWD of PMMA obtained is due to the less pronounced ability of cumyl–CH_2-CH_2O^-,K^+ to aggregate with PMMA growing centers.

Polymerization with higher monomer concentrations (2 and 3 mol/L) is to be expected with greater experimental errors, due to the inefficient reaction heat transfer. The local overheats lead to a significant increase of side reactions, an increase of the MWD, and an increase of the apparent initiator efficiency, respectively. The MWD becomes bimodal (Figure 2). The observed changes in the character of the MWD of the polymers can be explained

Table V
MWD of PMMA Prepared in EO (Experiment Nos. 16, 17, and 19, Table III)

					high MW[a] fraction		low MW[a] fraction	
no.	yield, %	M_{theor}	$\bar{M}_n$	M_w/M_n	$\bar{M}_n$	M_w/M_n	$\bar{M}_n$	M_w/M_n
17	10	5 900	17 500	2.7				
18	42	24 000	24 000	10.1	280 000	1.9	16 000	3.2
20	100	53 500	51 000	11.6	366 000	2.3	33 000	2.5

[a] Data obtained by differential curve resolving of GPC traces.

Table VI
Dependence of the PMMA Tacticity on the Nature of the Solvent (Initiator, t-BuOK)

solvent	polymn temp, °C	tacticity, % mm	mr	rr	ref
THF	−60	9	52	39	*a*
EO	−55	2	36	62	*a*
EO	−30	5	40	55	*a*
EO	0	5	39	56	*a*
DO	13	14	56	30	13
toluene + crown-6	−40	2	32	66	24
toluene	−40	39	35	26	24

[a] This work. [b] Crown-6–dicyclohexyl-18-crown-6.

not only by the existence of two types of AC with a low rate of equilibrium but also by the increased side reactions. The accumulation of a low molecular fraction up to 40% conversion (Table V) indicates that associated and nonassociated AC and terminated macromolecules are present in comparable amounts, the propagation rate constant of the associates being with orders of magnitude lower than that of the nonassociated AC.

The polymerization kinetics is very complicated. The first-order kinetics

$$\ln [[M]_0/[M]_\tau] = k_p C^* t$$

can be applied only for a real living polymerization process where C^* is constant. In our case the increase of the initiator efficiency with conversion (experiments with $[M]_0 = 1$ mol/L) shows that new polymer chains are constantly generated during the propagation. When the concentration of living ends is calculated by $C^* = [M]_0 x_p/\bar{P}_n$, the very approximate rate constant of propagation k_p^{app} = (−55 °C) lies between 0.04 and 2.0 $L \cdot mol^{-1} \cdot s^{-1}$. This value is 3–4 orders of magnitude lower than the rate constants in THF[12,22] and is in contradiction with the comparatively high polarity of the solvent. The rate of polymerization is so slow that it cannot compete with the rate of interconversion between different types of AC. Such a result accounts for two solvating effects of the growing polymer chains. The process proceeds in the presence of alkoxides, which form mixed associates with the growing ends and decrease the polymerization rates. (In the case of t-BuOLi, the rate constant decreases by a factor of 10.[23]) The small-sized molecule of EO also forms stable solvates with the growing AC. As frequently speculated, the oncoming MMA molecule has to displace a solvent molecule or unreacted alkoxide to form an intermediate complex with the growing ion-pair center. The stronger the interactions solvent (or alkoxide)–ion pair are, the more difficult is the formation of the intermediate complex with the monomer.

PMMA obtained with t-BuOK in EO is characterized by high heterotacticity. The propagation is consistent with Bernoullian statistics. The value of the persistence ratio ρ is close to 1. However, the significant difference in the distribution of the triads in THF and in EO solvents is worth mentioning (Table VI).

III. Synthesis of PMMA–PEO Block Copolymers. The block copolymers are usually obtained by means of anionic polymerization of MMA initiated by poly(ethylene glycol) alkoxides.[25-27] We tried the synthesis of a diblock copolymer by polymerization of EO using the potassium salt of PMMA in the presence of the monomer (EO) as a solvent. The main side reaction already mentioned is the intermolecular transesterification. This grafting can proceed between t-BuO(MMA)$_x$(EO)$_y$$CH_2CH_2O^-$,$K^+$ macromolecules. Another possibility for the formation of graft copolymers also exists. Unreacted t-BuOK can initiate homopolymerization of EO, followed by grafting the growing PEO chains to the ester functions of MMA units. A similar reaction has already been reported by Twaik et al.,[28] who had prepared poly(methyl methacrylate-*g*-ethylene oxide) from PMMA and the alkoxide derivative of PEO. Graft reactions proceed more readily with heavy alkali-metal alkoxides, the way it is in this instance. The experimental results are summarized in Table VII.

Table VII
Anionic Block Copolymerization of $PMMA^-$, K^+ and EO in EO (Initiator, t-BuOK; $[In]_0$ = 0.005 mol/L; $[MMA]_0$ = 2 mol/L; Polymerization of MMA, 1 h at −30 °C; Polymerization of EO, 24 h at 20 °C)

fraction	yield,[a] %	$\bar{M}_n$ (GPC)	EO/MMA NMR	tacticity, % mm	mr	rr
soluble						
benzene	3.6	8500	2	23	32	45
methanol	5.4	8000	1.9	6	27	67
insoluble						
gel	36			4	36	60

[a] Yield = polymer (g)/$[MMA]_g$ + $[EO]_g$ × 100. The ratio EO/MMA was determined by the intensities of CH_3O (3.60τ) and CH_2O (3.64τ).

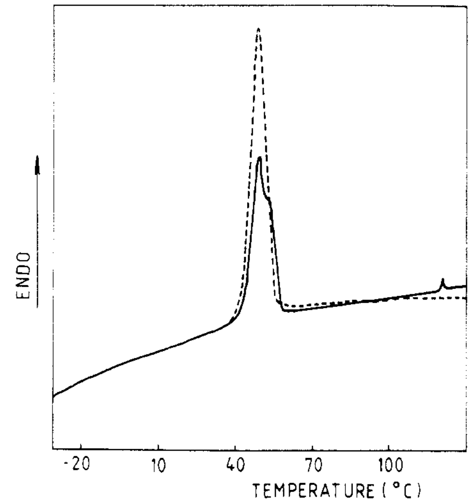


Figure 3. DSC thermograms of PMMA–PEO block copolymers: (—) methanol-soluble product; (- - -) benzene-soluble product.

The product was extracted thoroughly with methanol and benzene. Both fractions give fine emulsions in water, due to their surface-active properties. Infrared and NMR spectra of the methanol and the benzene fractions show the presence of both PEO and PMMA blocks of an almost equal EO/MMA ratio. Homopolymers are not detected

Table VIII
Anionic Polymerization of 2-VP in EO at −70 °C (Reaction time, 60 min)

initiator	$[2\text{-VP}]_0$, mol/L	$[\text{In}]_0 \times 10^3$, mol/L	yield, %	$\bar{M}_n$	M_w/M_n	efficiency	tacticity mm	 mr	 rr
OStLi	1.02	4.66	98	48700	1.6	0.44	35	53	12
OStLi	1.31	10.8	96	52000	1.5	0.23			
OStLi	0.51	3.5	100	56500	1.3	0.26			
CumK	0.42	5.56	98	20000	1.4	0.37	33	57	12
CumK[a]	1.38	6.00		15500			32	58	10
PycLi[b]							44	47	9
PycLi[c]							56	31	13
K^+ (THF)[d]							50	36	14

[a] Block copolymer with EO. [b] In THF, −78 °C.[37] [c] In toluene, −78 °C.[40] [d] −78 °C in THF.[40] The tacticity was determined according to ref 41.

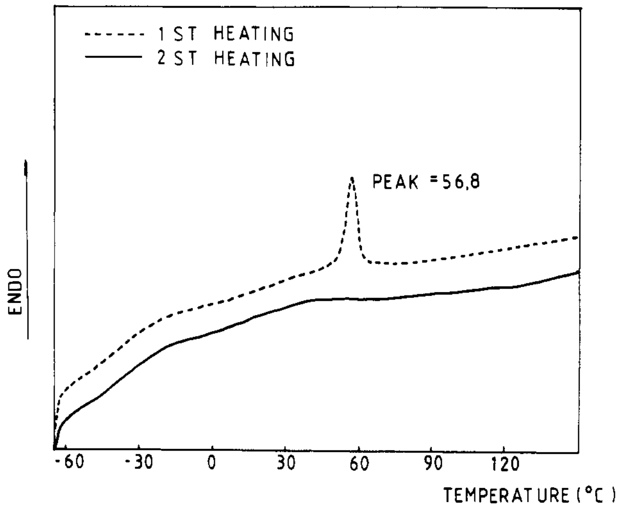


Figure 4. DSC thermograms of a PMMA–PEO network.

by GPC. It should be noted that the benzene-soluble block copolymer shows a larger proportion of isotactic triads. This finding indicates that the polymerization of MMA initiated by t-BuOK in EO involves at least two different growing centers. Transesterification reaction proceeds more easily with predominantly syndiotactic PMMA, due to steric reasons. As seen from Table VII, the methanol-soluble fraction and the insoluble gel fraction are poor in isotacticity. Most probably, the methanol-soluble fraction represents micelles formed after grafting between living oxirane chains and PMMA block sequences. This assumption finds support in DSC measurements of methanol- and benzene-soluble copolymers (Figure 3). DSC traces of methanol-soluble copolymer show two melting points due to PEO sequences with different M_n and different structure (block and graft).

The main product which is formed is an insoluble polymer network containing PMMA and PEO blocks. All attempts made to destroy the gels have failed. The gel is very stable against Soxhlet extraction in toluene or acidic and alkali treatment such as long-lasting heating (24 h) in dioxane–*p*-toluenesulfonic acids, HCl–water, and NaOH–water systems. At first glance, it is not easy to understand why this gel comprises up to 80% or more of the polymer. At room temperature only a negligible formation of a methyl ester group is transesterified with alkoxide potassium salt (intensities of CH_3 and CH_3O resonances in NMR spectra are almost equal). In this way some of the macromolecules may become very large with block and graft sequences. The light branching by chain transfer alone cannot produce an infinite network structure; thus, secondary chemical reactions cannot be responsible for gel formation. According to Gramain and Frere,[29,30] gel formation is due to structural factors leading to physical entanglements or partial crystallization promoted by the high packing of the polymers together with the presence of long grafts of PEO, which can show very strong intra- and intermolecular interactions.

PEO and MMA alone form "blends" with weak interactions approaching those of the van der Waals type.[31] Since DSC measurements (Figure 4) show two glass transition points (T_{g1} = 25.3 °C; T_{g2} = 31.3 °C), it is clear that a PEO-*b*-PMMA-*g*-PEO-*b*-PMMA network cannot be considered as a simple binary mixture. This result suggests the presence of two PEO–PMMA phases. The PEO crystalline phase disappears after the first heating in accordance to the previous results[32,33] that PEO and PMMA are miscible on the segmental level.

Swelling experiments were performed in order to gain more information on the morphology of the PEO–PMMA network. Benzene was used as a good solvent for both polymer components and water as a solvent for the polyether and a nonsolvent for PMMA. The PMMA–PEO (1:2) gel is predominantly hydrophobic according to the swelling power in H_2O and benzene:

	swelling power Q benzene	 H_2O
PMMA–PEO (1:2) gel	25	2
PEO–network	16	25

The irradiation dose is 5 Mrad.[34]

The swelling ratio Q is defined as $Q = V/V_0$, where V is the volume of the swollen gel and V_0 is the initial volume of the dry network. Because benzene is a good solvent for both polymer compounds, Q should be a measure of the cross-link density. As expected from Q, the PMMA–PEO network is very loose. The most significant observation is that the network has a very low degree of swelling in water, although the PEO content prevails. One possible explanation is the shielding effect of -*g*-PEO-*b*-PMMA hydrophobic chains which hinders the penetration of water into the PEO domains.

IV. Polymerization of 2-Vinylpyridine. There has been increased interest in recent years in the anionic polymerization of 2-vinylpyridine. The stereochemistry of 2-VP oligomerization was thoroughly studied.[35-37] With the aid of careful conductivity measurements on living polymers of 2-VP, Fischer and Szwarc[38] and Tardi et al.[39] independently showed that the counterion is most likely coordinated with the nitrogen lone pair of the penultimate pyridine ring. The variety of anionic initiators enables one to control the rate of the polymerization and the microstructure of the polymeric product. The polymerization of 2-VP in EO was carried out with oligostyryllithium (OStLi) and cumylpotassium (CumK) initiators. The main reason for this choice is to compare the effect of two cations with largely different coordination capacities on the intramolecular complexation with the penultimate pyridine ring. The experimental results are given in Table VIII.

Polymers of 2-VP obtained in EO with Li and K counterions are predominantly heterotactic–isotactic at the triad level, without any significant difference. This means that cation coordination is not linked with the stereoselectivity of the propagating centers. The isotacticity diminishes in the order toluene > THF > EO, which demonstrates the strong solvating power of EO.

The highly delocalized living poly(vinylpyridine) carbanion with a potassium counterion is capable of reacting with EO, thus forming block copolymers. According to DSC analysis, the crystallizable PEO block separates in a distinct phase. A preliminary electron microscopic study (TEM) on an OsO_4-stained sample of a PEO/P(2-VP) block with composition EO/2-VP = 4 shows that the polyether phase forms a continuous structure where dark domains of stained PVP are dispersed.

Conclusion

EO can be used as a strongly solvating medium in the anionic polymerization of polar vinyl monomers. The rate of the MMA polymerization initiated by t-BuOK is 3–4 orders of magnitude lower than in the THF. This is quite unexpected for a solvent of high solvating power and a high dielectric constant. Presumably, the oncoming monomer molecule cannot effectively compete with the associated alkoxide and peripherally bound EO molecules for the formation of an active center–monomer intermediate. The broad MWD and the formation of two types of block copolymers (according to PMMA block tacticity) suggest that propagation occurs on at least two types of active centers.

The polymerization involves some secondary transesterification reaction more pronounced by organopotassium initiators. Anionic polymerization of MMA in EO at temperatures higher than 0 °C results in loosely crosslinked but stable PMMA–PEO networks with amphiphilic properties.

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Registry No. α-LiEtIB, 143969-76-0; *t*-BuOK, 865-47-4; OStLi, 36345-04-7; PEO/2-VP (block copolymer), 143969-90-8; MMA, 80-62-6; EO, 75-21-8; PMMA, 9011-14-7; (MMA)(EO) (block copolymer), 108967-97-1; 2-VP (homopolymer), 25014-15-7; cumylpotassium, 3003-91-6; cryptand 222, 23978-09-8; 6-dicyclohexyl-18-crown-6, 16069-36-6.