

Tetrabutylammonium Benzoate-Initiated Polymerization of Propylene Oxide

XUEMIN CHEN and M. R. VAN DE MARK*

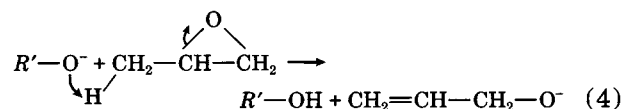
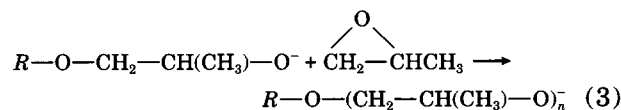
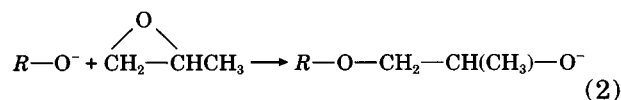
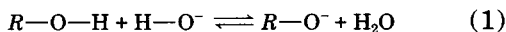
Department of Chemistry, University of Missouri-Rolla, Rolla, Missouri 65401

SYNOPSIS

The polymerization of propylene oxide by the benzoate anion was aided through the use of the tetrabutylammonium counterion. The effect of the tetrabutylammonium ion was to increase the solubility of the salt and to increase the ion separation. The polymerization was carried out in a pressure reactor at temperatures from 40 to 108°C, producing polymer yields of 2–78%. The study addressed the general effects of solvent, temperature, and ratio of initiator to monomer. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The polymerization of propylene oxide through anionic, cationic, and coordinate mechanisms has been the subject of numerous investigations.^{1–4} The accepted mechanism for the commercial polymerization of propylene oxide under caustic conditions is as follows²:



At room temperature or below, sodium and lithium hydroxides and alkoxides do not produce polymer. If the counterion is potassium, polymer is formed above 0°C (but only very slowly) and none is formed at lower temperatures.³ The initiation with either hydroxide or an alkoxide was extremely slow and

attack has been found to highly favor the primary epoxy position (110:3).^{5,6}

An important side reaction in the anionic polymerization of propylene oxide is shown in eq. 4, the abstraction of a proton to produce the allyl alkoxide.^{3,4} The reaction has been noted by numerous investigators, with the alkene being readily detected in the infrared and proton NMR spectra.^{3,7}

The alkali metal salts of carboxylic acids have been shown to be relatively unreactive as an anionic initiators for the polymerization of propylene oxide. However, carboxylate salts in the presence of crown ethers have been shown to produce polymers of oxiranes such as propylene oxide.^{7,8} Utilization of the potassium salt of carboxylic acids and the addition of a crown ether, 18-crown-6, allows the reaction to proceed under relatively mild conditions, 30–80°C in THF or neat. The crown ether forms a complex with the cation and allows increased solubility and ion separation, thus increasing its reactivity.⁷ Becker and Wagner investigated the effect of added crown ether on the polymerization of propylene oxide initiated by alkali metal alkoxides. It was found that the addition of crown ethers increased the charge separation of alkali metal alkoxides in organic media.⁹

Tetraalkylammonium salts of carboxylates in polar organic solvents have been demonstrated to be effective anionic initiators for the polymerization of strained ring lactones such as pivalolactone.^{10–12} The bulky organic tetraalkylammonium cations, which act analogously to the crown ethers, facilitate

* To whom correspondence should be addressed.

the charge separation of the ions as well as increase the salt's solubility in the organic media.

The study reported here addresses the use of the tetrabutylammonium ion as the counterion to a benzoate anion, a carboxylate anion, to initiate the polymerization of propylene oxide. The effects of temperature, reaction time, solvent, and initiator/monomer ratios were investigated. The yield, molecular weight, and spectral characteristics of the resultant polymers are herein discussed.

EXPERIMENTAL

The monomer, propylene oxide, was obtained from Arco and dried over calcium hydride, distilled, and stored over 4 Å molecular sieves. Acetonitrile was dried over P₂O₅ and distilled, dioxane and cyclohexane were dried over calcium hydride and distilled, and tetrahydrofuran was refluxed over sodium and distilled. Tetrabutylammonium benzoate was prepared by neutralization of tetrabutylammonium hydroxide with benzoic acid. The resultant wet salt was dried under vacuum at 0.01 mmHg at 53°C for 24 h.

The polymerizations were carried out in a small steel pressure reactor. The initiator, solvent, and monomer were introduced into the reactor under a blanket of dry argon. The reactor was closed and placed into a thermostated heater at the desired temperature. After completing the reaction, the product was neutralized with 20 μL of dilute HCl and the solvent and unreacted monomer were removed under vacuum (100 mmHg) and the residue

weighed. The polymers were characterized by ¹H-NMR, FTIR, and GPC.

The molecular weight was determined using gel permeation chromatography (GPC) with THF as the solvent. The system consisted of a Waters HPLC system with a refractive index detector, Apple II computer, and a 1000 and 10,000 Å 25 cm × 8 mm Styrogel columns in a series. The flow rate was 1 mL/min. The molecular weights are relative to polystyrene standards.

Polymerization of Propylene Oxide in Dioxane at 85°C

To the reactor were added under a blanket of dry argon 0.051g (0.14 mmol) tetrabutylammonium benzoate, 1.50 ml (21.5 mmol) propylene oxide, and 1.50 mL dry dioxane, and then the reactor was sealed. The reactor was heated for 40 h at 85°C. The reactor was then cooled and opened, and the contents transferred to a round-bottom flask and neutralized. The solvent and unreacted monomer were removed at reduced pressure. The residue was an amber liquid, 0.376 g (28.8% yield). The residue was then analyzed by NMR, IR, viscosity, and GPC.

RESULTS AND DISCUSSION

The initiation of the polymerization of propylene oxide by the tetrabutylammonium salt of benzoic acid was initially surveyed as to solvent effects. Table I shows the results of the study. Acetonitrile as

Table I Solvent Dependency for the Polymerization of Propylene Oxide^a

Solvent	Temperature (°C)	Reaction Time (h)	Yield (%)	M_n/M_w	e^b	δ_H^c
None	85	40	40.0	868/1047	8.2 ^d	18.8
Dioxane	85	40	28.8	591/801	5.2	19.7
	108	40	13.8	—	5.2	19.7
Cyclohexane	85	40	20.4	698/885	5.1	17.8
THF	85	40	18.8	—	7.9	18.7
Acetonitrile	85	40	57.4	890/1001	22.3	21.6
Acetonitrile ^e	85	40	12.4	—	—	—
Acetonitrile ^f	85	40	16.5	—	—	—

^a The initiator concentration, tetrabutylammonium benzoate, was 0.14 mmol.

^b Estimated dielectric of mixed solvent at 25°C based on volume average.

^c Hildebrand value based on volume average.

^d At 65°F; ref.: Dow Chem. Co. Tech. Info. Center.

^e With 0.195 g added water.

^f With 0.012 g added water.

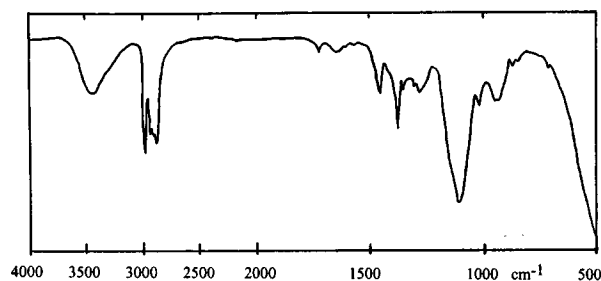


Figure 1 Infrared spectra of poly(propylene oxide) using the benzoate initiator in acetonitrile.

the solvent and propylene oxide neat produced the highest yield of polymer. All reactions in Table I were carried out at 85°C for 40 h except one at 108°C in dioxane. The ratio of benzoate to propylene oxide was 1:154, which was equivalent to a molecular weight of 9000 daltons for the polymer if the propylene oxide strictly reacted with the benzoate-initiated chains. It should be noted that the molecular weight was approximately 600–1000 daltons at 50% conversion. The polymer should have been 4500 daltons at that degree of reaction. The molecular weight here is, however, consistent with literature reports using hydroxide, alkoxide, or similar initiators i.e., approximately 1000 Daltons. Therefore, four chain transfers must be occurring, on average, per benzoate chain initiated.

The infrared spectra of polypropylene oxide prepared at 85°C in acetonitrile as above is shown in Figure 1. The absorption bands at 1719 and 1642 cm^{-1} are consistent with the formation of a benzoate ester. The proton NMR shows bands at 7.85, 7.32, and 3.33; and a doublet at 1.1 ppm. These spectra were consistent with the structure and the incorporation of benzoate into the polymer. The integration was, as expected, equivalent to 1 benzoate to approximately 75 propylene oxides. The 75:1 ratio does not imply that the polymer is 4500 Daltons,

but only that the ratio was consistent with materials input.

There are many factors that can contribute to solvent effects. Table II lists the solvent parameters for propylene oxide and the solvents used in this study. Correlation with the classic Hildebrand or Hansen values appears to be minimal. The Hansen hydrogen-bonding parameter does correlate with the yield. However, the Crowley hydrogen-bonding parameter does not correlate. The Crowley value is taken from the infrared shift of the O—D bond in deuterated ethanol vs. in the solvent media. The Hansen value is empirically derived. The molecular dipole moment has virtually no correlation with yield or molecular weight.

The mechanism of the polymerization reaction involves the attack of an anion on the epoxide. This ionic intermediate should be affected by the solvent in accordance with Coulomb's law. The relative charge separation should increase with higher dielectric constant. The dielectric constant for propylene oxide is 8.2, and knowing the others, we can see that higher dielectric constant media promotes polymerization. However, the solvent dielectric is not simply the dielectric of the added solvent. The reaction was 50% solvent 50% propylene oxide. Therefore, for comparison, the volume average of the dielectrics should be used. These volume-averaged dielectrics are shown in Table I. Both yield and molecular weight are favored by higher dielectric constant, as might be expected based upon the proposed mechanism.

The separation of the ions in the media would reduce the steric bulk imposed by the tetraalkylammonium ion. The initial nucleophilic attack of the benzoate anion produces an alkoxide anion that is analogous to that produced by hydroxide, alkoxide, or any nucleophile on the epoxy ring. Therefore, only the initial step in the polymerization is affected by the choice of nucleophile.

Table II Pure Solvent Solubility Parameters

	Hansen				ϵ	δ_{hild}	δ_c	$\mu/10^{30}$
	δ_d	δ_p	δ_h	δ_t				
Propylene oxide	13.6	8.2	10.4	18.9	8.2	18.8	10.0*	6.00
Acetonitrile	10.3	11.1	19.6	24.8	37.5	24.3	6.3	13.00
1,4-Dioxane	16.3	10.1	7.0	20.7	2.2	20.5	9.7	1.30
THF	13.3	11.0	6.7	18.5	7.6	18.6	—	5.44
Cyclohexane	16.5	3.1	0.0	16.8	2.0	16.8	0.0	0.00

* Value is unknown but estimated from ethylene oxide value.

Table III Initiator Concentration Dependency in Acetonitrile^a

Initiator Concentration (mmol)	Temperature (°C)	Reaction Time (h)	Yield (%)	M_n/M_w
0.00	85	40	2.4	—
0.03	85	40	5.9	—
0.05	85	40	10.0	—
0.14	85	40	57.4	890/1001
0.22	85	40	77.5	969/1111
0.44	85	40	75.3	473/553

^a Reaction media was 1.5 mL acetonitrile and 1.50 mL propylene oxide.

The pressure of the reactor was not monitored; however, the pressures in all the reactions were different due to the volatility of the materials. In all cases, the pressure was due mainly to the propylene oxide with a boiling point of only 34°C. The effect of pressure on polymerization reactions is to usually increase the rate, molecular weight, and the yield of polymer formation. Increases in pressure did not give a corresponding increase in yield. In addition, the molecular weight did not increase as a function of the temperature or calculated pressure increase as shown in Table IV. The detailed understanding of the effects of pressure would require external pressure and careful monitoring.

The addition of water radically reduces the yield of polymer. In the polymerization of propylene oxide with alkoxides, it has been shown that the addition of free alcohol increases the rate and yield of the reaction. It should be noted that a similar weak acid salt, sodium phenoxide, does not react with ethylene oxide below 80°C in the absence of free phenol.¹³ Here, water retards the reaction even though water has a high dielectric constant. Since benzoic acid is a weak acid, there exists an equilibrium with water and the benzoate ion to yield hydroxide. It is this

hydroxide that must be taking part in the reaction to some extent. The growing chain would also undergo chain transfer to water creating a hydroxide ion that could initiate additional short chains that may be volatile. After initiation, the propagating species is an alkoxide which is a very strong base. With water present, the propagating species would be effectively killed or at least transferred to the hydroxide.

The use of 0.14 mmol of benzoate as the initiator produced five times more chains than predicted at 0.64 mol % initiator. This number was based on the molecular weight coupled with initiator concentration and yield. There appears to be an effective chain-transfer mechanism operable. To evaluate this behavior, the initiator ratio was varied from zero to 2 mol % as shown in Table III. The yield of polymer tracks the amount of initiator up to 0.22 mmol. At 0.44 mmol initiator, the yield was approximately equal to that at 0.22 mmol; however, the molecular weight dropped from 969 to 473, which was consistent with the amount of initiator increase. The polymer molecular weights for the 0.14 and 0.22 mmol initiators are too similar to make any conclusive statements.

Table IV Temperature Effects on the Polymerization of Propylene Oxide^a

Initiator Concentration (mmol)	Temperature (°C)	Reaction Time (h)	Yield (%)	M_n/M_w
0.14	40	40	6.6	—
0.14	52	40	11.9	—
0.14	60	40	14.6	812/904
0.14	85	40	57.4	890/1001
0.14	95	40	61.9	738/894
0.14	108	40	31.0	869/961

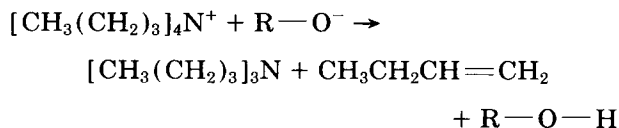
^a Reactions were carried out in 50% acetonitrile as the solvent.

Table V Polymerization of Propylene Oxide as a Function of Time^a

Initiator Concentration (mmol)	Temperature (°C)	Reaction Time (h)	Yield (%)	M_n/M_w
0.14	85	20	43.8	845/955
0.14	85	31	45.2	700/849
0.14	85	40	57.4	890/1001
0.14	85	50	57.6	808/946
0.14	85	64	59.5	—

^a Reactions were carried out in 50% acetonitrile as the solvent.

The effect of temperature was evaluated from 40 to 108°C. As can be seen from Table IV, the yield of polymer increases from 40 to 95°C. At 108°C, the yield drops to 31% but the molecular weight remains constant. The molecular weight was relatively independent of temperature. The drop at 108°C may be simply the degradation of the quaternary salt as shown below. This side reaction would cause a loss of initiator and the production of volatile products.



The time dependency of the reaction was studied from 20 to 64 h. Table V shows that the reaction was relatively independent of time above 40 h. The molecular weight appears to be independent of time, which implies that the initiation was relatively slow but that the propagation step was fast. If the terminal end was a hydroxyl group, chain transfer from another anion would have been possible. If virtually all the terminal groups were hydroxy groups and, as with other alkoxides, proton exchange would be very rapid, the chain transfer from chain to chain would maintain equal reactivity of the chains and keep the polydispersity low.

The molecular weight distribution in all cases was quite narrow; typically, the polydispersity ranged between 1.12 and 1.21 in acetonitrile media. This type of polydispersity was consistent with the pro-

posed polymerization process where all species had equal reactivity once initiated.

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