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Notes

Telechelic Polymerization of Epichlorohydrin Using 1,4-Butanediyl Ditriflate as the Initiator

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Previous studies of cationic polymerization of epichlorohydrin (ECH) indicate that commonly used initiator systems, Lewis acid/alcohol or tertiary oxonium salt/alcohol complexes, give poly(epichlorohydrin) (PECH) with average molecular weight less than 4000 and with terminal groups that are primarily secondary alcohols.[1-3] If telechelic PECH with varying molecular weight in the range 4000–15 000 and with various functional groups can be synthesized, there is the potential for a broad range of applications. A polymerization system with this potential was discovered when 1,4-butanediyl ditriflate (BDT) was used as the initiator.

Experimental Section

Epichlorohydrin and dichloromethane were distilled from calcium hydride, and tetrahydrofuran (THF) and dioxane were distilled from lithium aluminum hydride under a nitrogen atmosphere. Ethyl triflate (ET) (99% purity, Aldrich Chemical Co.) was used without further purification.

1,4-Butanediyl ditriflate (BDT) was synthesized from THF and trifluoromethanesulfonic anhydride (T_fOT_f). To a flame-dried, 500-mL three-neck flask (equipped with a 50-mL addition funnel, thermometer, argon inlet tube, and a magnetic stirring bar) were added 150 mL of dichloromethane, 1.0 g (0.024 mol) of calcium hydride powder, and 100 g (0.354 mol) of T_fOT_f (Aldrich Chemical Co., used without further purification). After the dropwise addition of 30.7 g (0.425 mol) of THF at 0 °C, the reaction mixture was allowed to warm to room temperature. After the volatiles were removed in vacuo, the crude product was recrystallized from dichloromethane, yielding 83.7 g (68%) of colorless crystals; mp 35–36 °C, purity 98% (based on GPC). Anal. Calcd for $C_6H_8F_6O_6S_2$: C, 20.3; H, 2.3; F, 32.2; S, 18.1. Found: C, 19.85; H, 2.42; F, 32.20; S, 18.00. ^{1}H NMR (in C_6D_6): 3.73 (4 H, m), 1.01 (4 H, m) ppm. ^{13}C proton-decoupled NMR: 25.1 (s), 76.1 (s), 119 (q) ppm. IR (in CCl_4): 1427, 1220, 1146, 920 cm^{-1}.

Polymerization of ECH. A typical polymerization procedure is as follows. To a flame-dried, 250-mL single-neck flask were added 0.228 g (0.011 equiv) of calcium hydride, 3.83 g (0.0216 equiv) of BDT, 10 g of dichloromethane, and 20.0 g (0.216 equiv) of ECH. The reaction flask was placed in a 25 °C oil bath equipped with an automatic shaker and allowed to shake for 24 h under an argon atmosphere. The reaction mixture was then treated with the desired terminating agent.

Termination Reaction of PECH. The polymerization mixture was filtered to remove calcium hydride, and the filtrate was slowly added to a stirred solution of the appropriate terminating agent under a nitrogen atmosphere. The resulting mixture was placed in a 30 °C oil bath equipped with an automatic shaker and shaken for 1–3 days. It is important that the terminating agent is soluble in the PECH solution; otherwise a complete termination reaction is difficult to achieve. A trace of unreacted triflate ester appears to cause a slow degradation of the polymer at 90 °C. Dioxane was found to be the best cosolvent. The terminating agents, (1) potassium phenoxide and (2) calcium or lithium alkoxide, in the amounts of a tenfold stoichiometric excess based on the BDT were used.

Purification (Fractionation) of Terminated PECH. The reaction mixture was filtered if solids were present, and the organic layer (polymer solution) was separated if there were two layers. After the polymer solution was washed with water until the wash water was neutral, the solvent was removed with a rotary evaporator at 40–45 °C. The residual polymer was washed three times with cold methanol and then dissolved in a minimum amount of toluene followed by rotary evaporation of this solution using the vacuum of an oil pump at 50 °C until its weight remained constant. The substantial removal of methanol was assured by GPC and NMR analyses. It was critical that the methanol was removed as completely as possible; otherwise a false equivalent weight determination would result.

Polymer Characterization. (1) Average molecular weight and polydispersity were determined by gel permeation chromatography (GPC) using THF as the eluent and PECH (Polysciences) and polystyrene (Pressure Chemicals) as standards.

(2) The hydroxy equivalent weight of PECH was determined by a physical method in which the THF-associated OH peak was monitored by infrared spectroscopy.[4]

(3) ^{13}C NMR analysis was carried out as follows: The hydroxy end groups were derivatized by allowing a mixture of 500 mg of polymer, 2 mL of trifluoroacetic anhydride, and 2 mL of pyridine to stir overnight. After the volatiles were removed under vacuum, the residue was triturated twice with 1-mL portions of benzene-d_6. Then the combined 2 mL of benzene-d_6 solution of the trifluoroacetate derivative was used to determine the ^{13}C NMR spectrum. The ^{13}C NMR spectra were obtained at 20 MHz with a Varian FT-80A spectrometer, 10-mm sample tubes, and solutions that were 20–30% sample dissolved in benzene-d_6. It was necessary to accumulate 10 000–15 000 transients with the following spectrometer operating conditions: 4-kHz spectral width, 16K data table, 45° pulse, 3-s pulse repetition rate, and maximum power broad-band decoupling with a 1-kHz bandwidth.

Results and Discussion

Results on polymerization of ECH using BDT and ethyl triflate (ET) are summarized in Table I. Both initiators give about the same results based on the monomer/initiator equivalent ratio, and PECH with molecular weights as high as 15 000 can be obtained.

For the end-group analyses, the polymerization mixture was divided into two portions. (a) One was treated with 1,4-butanediol in the presence of a stoichiometric excess of calcium hydride, and (b) the other portion was treated with potassium phenoxide.

(a) PECH Terminated with 1,4-Butanediol (PECH-OH). The end groups were analyzed by comparing the ^{13}C NMR spectra of PECH and its trifluoroacetate derivative. The peak assignments were made by utilizing the spectra of PECH from Minnesota Mining and Manufacturing (3M) and poly(tetrahydrofuran) (PTHF) from Du Pont, whose end-group structures have been well characterized (Figure 1). These assignments are based on the deshielding effect of hydroxy groups on neighboring carbons as well as a comparison of the chemical shift of these carbons when the hydroxy groups are converted to the trifluoroacetate derivatives. The δ-values of the internal carbons of the polymeric chains are not significantly affected by the derivatization, but those of the end groups shift significantly. The general trends in the

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Table I
Polymerization of ECH under Various Conditions

item	init (I)	[I]/[M]^a	reacn temp (°C)/ time (h)	% yield^b	$\bar{M}_n$(GPC)^c
1	ET	1/10	40/17	35	3400
2	ET	1/20	40/17	35	7000
3	BDT	1/10	40/17	40	6400
4	BDT	1/10	25/24	50	6900
5	BDT	1/20	25/17	20	15000

[a] [I]/[M] = equivalent ratio. [b] Yield after purification. [c] Number-average molecular weight of purified (fractionated) PECH (GPC using PECH and polystyrene standards as reference in THF).

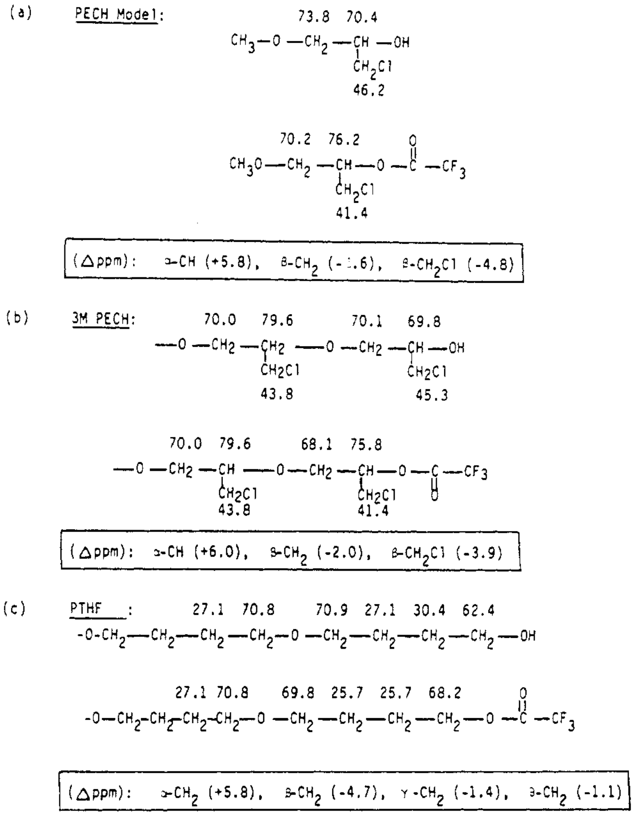
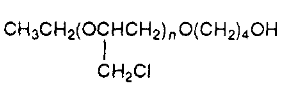


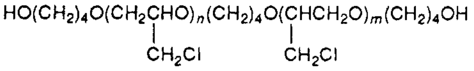
Figure 1. ^{13}C NMR (20% in C_6D_6) of various end groups (ppm from TMS): change in chemical shifts (Δppm) of neighboring carbons when the alcohols are converted to the trifluoroacetates.

change of the chemical shifts of the end carbons are such that the α-carbons are strongly deshielded (+6 ppm), the β-carbons shielded (-3 to -5 ppm), and γ- and δ-carbons slightly shielded when the alcohols are converted to the trifluoroacetate derivatives.

Results of ^{13}C NMR spectra of our PECH-OH and their trifluoroacetate derivatives are shown in Figure 2. PECH-OH(I) was initiated by ET and PECH-OH(II) was initiated by BDT, with structures expected to be as follows:


$CH_3CH_2(O\underset{CH_2Cl}{CH}CH_2)_nO(CH_2)_4OH$

PECH-OH(I)


$HO(CH_2)_4O(CH_2\underset{CH_2Cl}{CH}O)_n(CH_2)_4O(\underset{CH_2Cl}{CH}CH_2O)_m(CH_2)_4OH$

PECH-OH(II)

The chemical shifts for the ethyl carbons at the head of the polymeric chain and the carbons of $CH_2CH_2CH_2OH$ at the tail along with the strong multiple peaks for the internal carbons of PECH-OH(I) are identified along with those of its trifluoroacetate derivative (Figure 2a). When the alcohols are derivatized the δ-values of the ethyl carbons (head groups) and the internal carbons of the polymeric chains remain approximately the same. However, the δ-value changes for the α-C (+5.9 ppm), β-C (-4.4 ppm), and γ-C (-1.6 ppm) were observed for the tail group. The shift trend for the peaks of these carbons is similar to that observed for the end groups of PTHF (Figure 1c). The spectra of PECH (Figure 2b) initiated by BDT, PECH-OH(II), are the same as those initiated by ET, except that the peaks for the ethyl groups in PECH-OH(I) have been replaced by the $OCH_2CH_2CH_2CH_2$ groups present in the middle of the polymer chains.

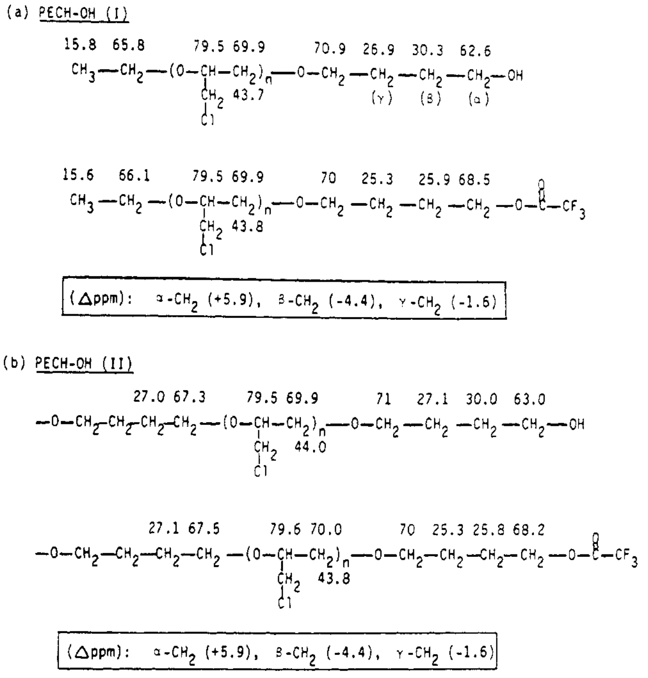


Figure 2. ^{13}C NMR (20% in C_6D_6) of PECH-OH: change in chemical shifts (Δppm) of neighboring carbons when the alcohols are converted to the trifluoroacetates.

Table II
Number-Average Molecular Weight and Equivalent Weight of PECH^a

item	init	terminating agent	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	OH equiv wt
1	ET	BD^b	3400	1.4	3610
2	BDT	BD	6400	1.5	3340
3	BDT	TMP^c	6400	1.5	1670

[a] Polymerization for 17 h at 40 °C in dichloroethane; [I]/[M] = 1/10. [b] 1,4-Butanediol. [c] Trimethylolpropane.

Additional evidence for the structures of PECH-OH-(I) and PECH-OH(II) comes from a comparison of the infrared spectra of the alcohol groups. The terminal groups of PECH-OH have the OH-associated bands at 3475 cm^{-1} in THF and 3618 cm^{-1} in CH_2Cl_2. These values are close to those of primary alcohol groups of PTHF (3480 cm^{-1} in THF and 3618 cm^{-1} in CH_2Cl_2) and are unlike those of secondary alcohols found in 3M PECH (3409 cm^{-1} in THF and 3571 cm^{-1} in CH_2Cl_2). Furthermore, the hydroxy equivalent weight determinations indicate that PECH-OH(I) is approximately monofunctional and PECH-OH(II) is difunctional (Table II). When PECH is initiated by BDT and terminated with trimethylolpropane, a triol, the polymer becomes tetrafunctional as expected (Table II, item 3).

(b) PECH Terminated by Phenoxy Groups (PECH-OPh). The end groups were analyzed by comparing UV and ^{13}C NMR spectra. The UV absorption bands of the

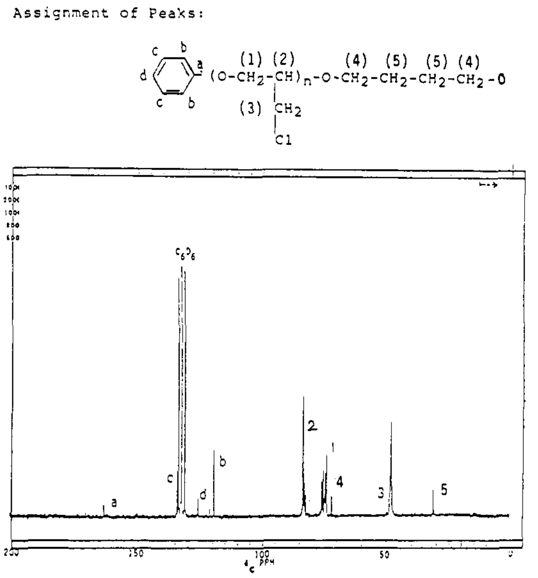


Figure 3. ^{13}C NMR of PECH terminated with potassium phenoxide (30% (w/w) in C_6D_6 at 25 °C).

phenoxy-terminated PECH (PECH-OPh) are similar to those of methoxybenzene. ^{13}C NMR spectra of the phenoxide-terminated PECH are consistent with the expected structure (Figure 3): When the spectra of PECH-OH-(II) and PECH-OPh are compared, the latter does not have peaks for the carbons $CH_2CH_2CH_2OH$ but has new ^{13}C peaks at 115, 121, 129.9, and 159.3 ppm. These peaks are assigned to the carbons of the phenyl ring using *n*-butyl phenyl ether as a reference.

End-group studies, as described in sections a and b, demonstrate that treatment of the polymerization reaction mixture with appropriate nucleophiles gives different end groups, without altering the PECH backbone. Hence, the polymerization and termination reactions in Figure 4 are consistent with the observed results.

PECH yields in these systems are only 35–50%, and therefore components of the remaining 50–65% are being identified. Furthermore, kinetics of polymerization and correlation of molecular weight with polymer conversion are currently being investigated in order to understand the polymerization mechanism.

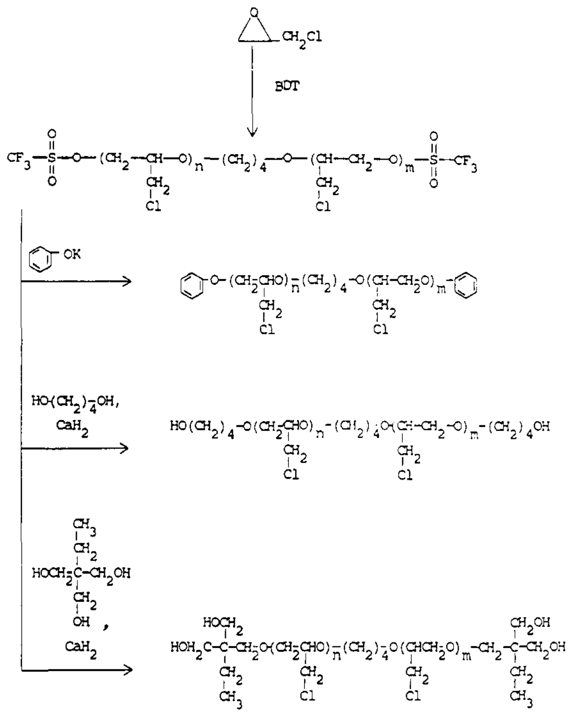


Figure 4. Polymerization and termination reactions of PECH.

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References and Notes

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Registry No. BDT, 18934-34-4; PECH-OH, 129124-09-0; PECH-OPh, 129124-10-3; PECH-trimethylolpropane, 129124-11-4.