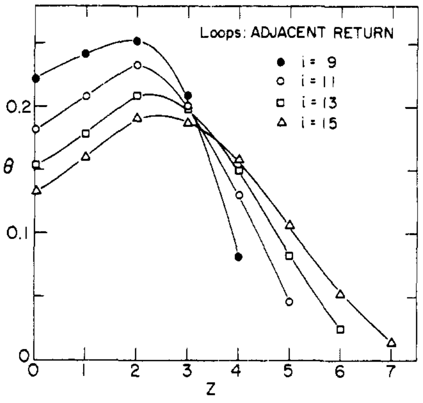

Figure 4. Plots of fraction of segments vs. normal to the surface distance for adjacently returning loops.

Table V
Estimates for the Fraction of Segments as a Function of the Distance Normal to the Surface for an Isolated Infinite Chain

z	Fraction	*z*	Fraction
0	0.00	4	(0.06—0.08)
1	0.01	5	(0.100—0.120)
2	0.03	6	(0.138—0.148)
3	(0.04—0.05)	7	~0.143

generalized shape is in agreement with that reported by Hesselink[2] and that computed from the data of Meier.[3] It did not seem worthwhile to make more quantitative comparisons considering the errors involved in our methods. It becomes clear that data for longer walks will be necessary to quantitatively describe the infinite chain in the vicinity of the maximum and at higher *z* levels. For the present we deemed it too difficult to obtain such data due to the enormous amount of computer time required.

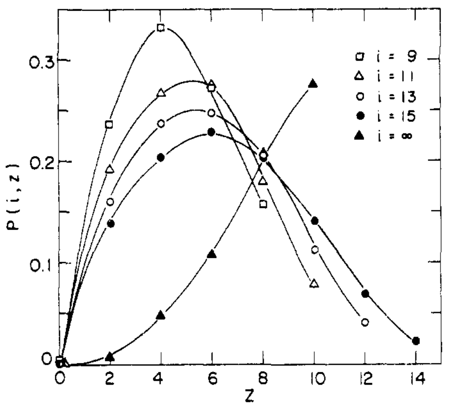

Figure 5. Plots of the probability for finding the chain end a distance *z* from the surface.

Figure 5 is a plot for chain ends. It should be noted that whereas the maximum density of chain segments for finite chains of size $i = 15$ are located in level 4, the maximum probability for finding the end point is in level 6. This means that in general the thickness of the chain film at distances beyond where the maximum density of segments occurs is determined primarily by chain ends.

The distribution of segments for a chain which may touch a surface with any of its segments has also been considered. The results for this particular model are being published separately.

References and Notes

(1) M. Lax, *Macromolecule*, **7**, 660 (1974).
(2) F. Th. Hesselink, *J. Phys. Chem.*, **10**, 3488 (1969).
(3) D. J. Meier, *J. Phys. Chem.*, **71**, 1861 (1967).
(4) A similar phenomenon is the well-known isosbestic point.

Communications to the Editor

Hydrogen-Transfer Polymerization of Hydroxyalkyl Acrylates

The present communication reports a base-catalyzed hydrogen-transfer polymerization of hydroxyalkyl acrylates (**1**) to produce polymers having an ester–ether type structure **2** (eq 1). Monomers examined were 2-hydroxyethyl

$$\mathrm{CH_2{=}CHCO_2{-}Y{-}OH} \xrightarrow{\mathrm{B:}} \text{-}\!\left(\mathrm{CH_2CH_2CO_2{-}Y{-}O}\right)\!\text{-}_n \qquad (1)$$

1a, Y = $\mathrm{CH_2CH_2}$ (2-HEA) **2a**
1b, Y = $\mathrm{CH_2CH_2CH_2}$ (3-HPA) **2b**
1c, Y = $\mathrm{CH_2CHCH_3}$ (2-HPA) **2c**

(2-HEA), 3-hydroxypropyl (3-HPA), and 2-hydroxypropyl (2-HPA) acrylates. This polymerization is regarded as being closely related to the base-catalyzed hydrogen-transfer polymerization of acrylic acid (eq 2) recently reported by us.[1]

$$\mathrm{CH_2{=}CHCO_2H} \xrightarrow{\mathrm{B:}} \text{-}\!\left(\mathrm{CH_2CH_2CO_2}\right)\!\text{-}_n \qquad (2)$$

A typical example of polymerization is as follows. A mixture of 1.64 g (15 mmol) of 2-HEA and 2.4 mg (2.0 mol % for 2HEA) of LiH was placed in a sealed tube under nitrogen and kept at 50°. As the reaction proceeded the system became viscous. After 100 hr the tube was opened and the polymeric material was dissolved in 8 ml of $\mathrm{CHCl_3}$. The solution was washed twice with 1 ml of $\mathrm{H_2O}$, dried on $\mathrm{K_2CO_3}$, and poured into a large amount of diethyl ether–hexane (50:50) mixture to precipitate the polymeric material. The polymer was isolated by decantation and dried in vacuo (1.52 g, 93% yield). It is a colorless paste, soluble in $\mathrm{CHCl_3}$, DMF, and other polar solvents but insoluble in $\mathrm{H_2O}$ and diethyl ether.

An ir spectrum of the polymer (Figure 1) shows the presence of ester (1735 $\mathrm{cm^{-1}}$) and ether (1180 $\mathrm{cm^{-1}}$) groups. It should be noted that the intensity of $\nu_{\mathrm{O-H}}$ at 3200–3500 $\mathrm{cm^{-1}}$ was greatly decreased in the polymer. The NMR spectrum of the polymer (Figure 2) shows a triplet (peak A at δ 2.58, $\mathrm{CCH_2CO_2}$, 2 H), a multiplet and triplet (peaks B and C at 3.54 and 3.70, respectively, $\mathrm{OCH_2C}$, 4 H), a multiplet (peak D at 4.25, $\mathrm{CO_2CH_2C}$, 2 H), and a multiplet (peak E at 6.4–5.5, $\mathrm{CH_2{=}CHCO_2}$). These data strongly indicate the polymer structure of **3a**. Based on the assumption that

$$\mathrm{CH_2{=}CHCO_2CH_2CH_2O}\text{-}\!\left(\mathrm{CH_2CH_2CO_2CH_2CH_2O}\right)\!\text{-}_{n-1}\mathrm{H}$$

3a

Table I
Hydrogen-Transfer Polymerization of 2-HEA by Various Base Catalysts[a]

No.	Catalyst (mol % for 2-HEA)	Solvent	Temp, °C	Time, hr	Yield, %	Mol wt NMR	Mol wt VPO	Anal.[b] % C	Anal.[b] % H
1	LiH (2.0)	DMF	50	100	93	2160	1980	51.49	6.78
2	*t*-BuOLi (2.5)		R.T.[c]	24	64		1540		
3	*t*-BuOLi (5.0)		50	20	66		1370		
4	NaH (3.0)		80	20	50		1080		
5	NaH (3.0)	THF	70	20	43		876		
6	MeONa (5.0)		80	20	61	2060		51.29	6.78
7	*t*-BuOK (5.0)		80	20	68	1430	1680		
8	Ph_3P (5.0)		80	40	65		1100	52.51	6.71

[a] 2-HEA = 1.64 g. Solvent = 1.0 ml. [b] Calcd for $C_5H_8O_3$: C, 51.72; H, 6.94. [c] R.T. = room temperature.

Figure 1. Ir spectrum of polymer **2a** from 2-hydroxyethyl acrylate (**1a**).

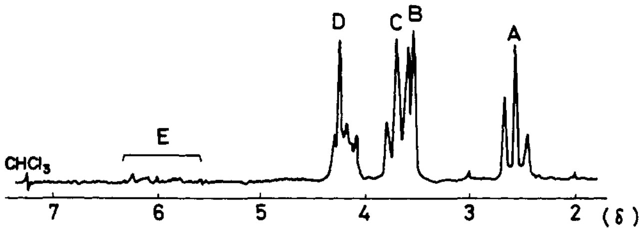

Figure 2. NMR spectrum of polymer **2a** (in $CDCl_3$).

a vinyl group is contained at each polymer end, the degree of polymerization ($\bar{P}_n$) was calculated from the integration value of peaks A (2 H) and E (3 H) to yield n = 18.6. This magnitude corresponds to the molecular weight of 2160, which is close to that obtained by vapor pressure osmometry, i.e., 1980. The elemental analysis of the polymer indicates the same composition as 2-HEA (No. 1 in Table I). No vinyl polymerization was observed under the polymerization conditions.

Hydrogen-transfer polymerization of 2-HEA was examined by several base catalysts under various reaction conditions (Table I). Hydrides and alkoxides of metals Li, Na, and K were effective catalysts for the polymerization of 2-HEA. Triphenylphosphine (Ph_3P) was also an active catalyst. The molecular weight of polymers was at most about 2000. Other base catalysts such as pyridine, dimethoxymagnesium, and triethoxyaluminum did not induce the polymerization of 2-HEA, i.e., most 2-HEA was recovered unchanged after the polymerization.

Hydrogen-transfer polymerization is not limited to 2-HEA. Hydroxylalkyl acrylates of 3-HPA and 2-HPA underwent the polymerization by a base catalyst (Table II), and the polymer structure was generally given by **2a–c**, respectively. The molecular weight of the polymer from 3-HPA was even higher than that from 2-HEA.

The present polymerization provides a novel method to prepare polymers of an ester–ether structure, e.g., **2a** can be regarded as an alternating copolymer of β-propiolactone and ethylene oxide.

Table II
Hydrogen-Transfer Polymerization of 2-HEA, 3-HPA, and 2-HPA[a]

Monomer	Time, day	Yield, %	Polymer structure	Mol wt[b]
2-HEA	2.0	67	**2a**	1150
3-HPA	2.0	94	**2b**	2290
2-HPA	30	59	**2c**	864

[a] Monomer = 15 mmol, *t*-BuOLi catalyst = 5.0 mol % for monomer. Bulk polymerization at R.T. [b] Determined by vapor pressure osmometry.

As to a mechanism, the following may be conceivable in the polymerization of 2-HEA catalyzed by LiH. The first formed alcoholate **4** adds to 2-HEA via Michael type addition to produce a transient carbanion **5**,

$$\underset{\text{2-HEA}}{CH_2{=}CHCO_2CH_2CH_2OH} + LiH \longrightarrow \underset{\mathbf{4}}{H_2C{=}CHCO_2CH_2CH_2O^-Li^+} + H_2 \quad (3)$$

$$\mathbf{4} + \text{2-HEA} \longrightarrow \underset{\mathbf{5}}{[CH_2{=}CHCO_2CH_2CH_2OCH_2C^-HCO_2CH_2CH_2OH \cdot Li^+]} \xrightarrow{\overset{+}{H}\text{ transfer}} \underset{\mathbf{6}}{CH_2{=}CHCO_2CH_2CH_2OCH_2CH_2CO_2CH_2CH_2O^-Li^+} \quad (4)$$

Generally

$$\sim\sim CH_2CH_2CO_2CH_2CH_2O^-Li^+ + \text{2-HEA} \longrightarrow [\sim\sim CH_2CH_2CO_2CH_2CH_2OCH_2\bar{C}HCO_2CH_2CH_2OH \cdot Li^+] \xrightarrow{H^+\text{transfer}} \sim\sim CH_2CH_2CO_2CH_2CH_2OCH_2CH_2CO_2CH_2CH_2O^-Li^+ \quad (5)$$

which abstracts a proton (through inter- and/or intramolecularly) to form again an alcoholate **6**. A general expression is given by eq 5.

Alternatively, a mechanism of the so-called polyaddition polymerization is also likely as considered in the hydrogen-transfer polymerization of acrylamide.[2] This point may be elucidated by an examination of the molecular weight distribution during polymerization. It is possible that the propagating alcoholate end attacks an ester group of polymer to bring about the C–O bond fission, which causes the molecular weight decrease of polymers.

It is interesting to note that Ph_3P can induce the polymerization of 2-HEA (No. 8 in Table I). After the polymerization a sample polymer (No. 8) in $CHCl_3$ was washed three times with H_2O. An NMR spectrum of the sample showed proton signals due to vinyl (δ 6.3–5.5) and triphenylphosphonium (δ 7.70) groups. Further washings did not decrease the intensity of the latter signal. This indicates that the polymerization system involved two types of propagating species, e.g., a macrozwitterion[3] **7** and a gegen-

$$\mathrm{Ph_3P^+CH_2CH_2CO_2}\sim\sim\sim\mathrm{CH_2CH_2O^-}$$

7

$$\mathrm{CH_2{=}CHCO_2}\sim\sim\sim\mathrm{CH_2CH_2O^-\cdot Ph_3P^+X}$$

8

(X = H or alkyl derivative)

ion[1] 8 species. By washing with H_2O the gegencation of 8 must be washed out,[1] whereas that of 7 is not. Coupled with this, an elemental analysis of the sample polymer showed a content in 0.52% of P. A molar ratio of 7 to 8 was calculated by NMR (15 H and 3 H, respectively) to be 1.0:2.9.

References and Notes

(1) T. Saegusa, S. Kobayashi, and Y. Kimura, *Macromolecules*, **7**, 256 (1974).

(2) D. S. Breslow, G. E. Hulse, and A. S. Matlack, *J. Am. Chem. Soc.*, **79**, 3760 (1957).

(3) T. Saegusa, S. Kobayashi, and Y. Kimura, *Macromolecules*, **8**, 374 (1975).

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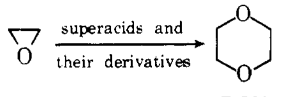
Superacids and Their Derivatives. IX.[1] Selective Cyclodimerization of Ethylene Oxide to 1,4-Dioxane Catalyzed by Superacids and Their Derivatives

Recently we have reported reactions of a series of cyclic ethers by means of superacids and their derivatives. In these works ring-opening polymerizations of seven-,[1] five-,[2-6] and four-membered cyclic ethers[7] and oxonium formation reactions of a six-membered cyclic ether[8] have been studied mainly from the kinetic and mechanistic viewpoints. Now we disclose, for the first time, that in the reaction of a three-membered cyclic ether, ethylene oxide (EO), catalyzed by superacids and their derivatives, selective cyclodimerization occurs to produce 1,4-dioxane (DON) in high yields (eq 1). Superacids are acids stronger than 100% sulfuric acid.[5,9] In the present study trifluoromethanesulfonic (CF_3SO_3H, TfOH), fluorosulfonic (FSO_3H), chlorosulfonic ($ClSO_3H$), and perchloric ($HClO_4$) acids were employed as the superacid components.



(1)

EO DON

A typical run (No. 10 in Table I) was as follows. Into a reaction tube containing 0.088 mmol of MeOTf 8.0 mmol of EO was introduced at −78° under nitrogen. The reaction tube was sealed and kept at 35°. After 16.5 hr EO was completely consumed (examined by ^1H NMR spectroscopy), and the reaction mixture was poured into a methanol solution of sodium methoxide at −30° to stop the reaction. All the volatile material was trapped by vacuum distillation. The GLC analysis of the distillate (chlorobenzene as an internal standard) showed that 0.33 g of DON was produced (95% yield based on the charged EO). Besides DON, small amounts of 2-methyl-1,3-dioxolane (~3.0%) and of ethylene and diethylene glycol ethers were produced.

Similarly, four superacids (No. 1–5), four superacid esters[5] (No. 6–13), and a superacid anhydride (No. 14) were employed as catalysts for cyclodimerization of EO under various reaction conditions (Table I). It is shown that superacids and their derivatives are effective and selective catalysts for the production of DON from EO. In the systems catalyzed by superacid esters and by the anhydride the yield and selectivity of DON were always high (except for No. 13). Although the conversion of EO was quantitative in the superacid catalyzed systems (except for No. 3), the yield of DON was relatively low. The other part of EO was converted into poly-EO. The reactions by $ClSO_3H$ and $MeOSO_2Cl$ gave low conversion of EO (No. 3 and 13). Under the reaction conditions Cl–S bond cleavage probably took place readily due to the reduced stability of the $ClSO_3^-$ group,[6] which brought about the termination of reaction. An aprotic polar solvent, nitromethane, accelerated the reaction whereas a less polar one, CH_2Cl_2, rather retarded the reaction (No. 6–8 and vide infra). In the above reactions 2-methyl-1,3-dioxolane was detected as a main by-product. The amount of the by-product, however, was at most 4% for DON under the present reaction conditions. For the sake of comparison Table I includes the results of the reactions of EO catalyzed by H_2SO_4 and MeOTs (No. 15 and 16). Neither catalyst yielded DON under these conditions. This finding indicates the difference in catalyst activity between superacids and strong acids of H_2SO_4 and TsOH.

The cationic ring-opening polymerization of EO was first achieved in 1933 by Staudinger and Lehmann with the use

Table I
Cyclodimerization of Ethylene Oxide Catalyzed by Superacids and Their Derivatives under Various Reaction Conditions[a]

No.	Catalyst	Mol % for EO	Solvent	Reaction temp, °C	Reaction time, hr	Conversion of EO, %	Yield of DON,[b] %
1	TfOH	(2.0)		20	13.5	100	80
2	FSO_3H	(2.5)		20	17.5	100	65
3	$ClSO_3H$	(4.7)	CH_2Cl_2	20	4	20	3
4	$TfOH{\cdot}H_2O$	(2.0)		20	5	100	30
5	70% aq $HClO_4$	(2.1)		20	5	100	20
6	EtOTf	(5.0)	CH_3NO_2	35	1.3	100	90
7	EtOTf	(5.0)		35	10	100	92
8	EtOTf	(5.0)	CH_2Cl_2	35	28	100	89
9	MeOTf	(1.1)	CH_3NO_2	35	4	100	96
10	MeOTf	(1.1)		35	16.5	100	95
11	MeOTf	(5.0)	CH_3NO_2	10	14.5	100	88
12	$EtOSO_2F$	(5.1)		35	13	100	90
13	$MeOSO_2Cl$	(5.1)		40	4	30	6
14	Tf_2O	(4.6)	CH_2Cl_2	40	10	100	91
15	95% aq H_2SO_4	(2.0)		20	5	16	0
16	MeOTs[c]	(4.7)	$C_6H_5NO_2$	40	10	0	0

[a] The charged EO was 8.0 mmol when bulk and 4.0 mmol in 0.20 ml of solvent when in solution. [b] Based on the charged EO. [c] Methyl *p*-toluenesulfonate.