

## SYNTHESIS AND PROPERTIES OF REGULAR COPOLYMERS—III

## REACTIONS INVOLVING EPICHLORHYDRIN AND DIEPOXIDES

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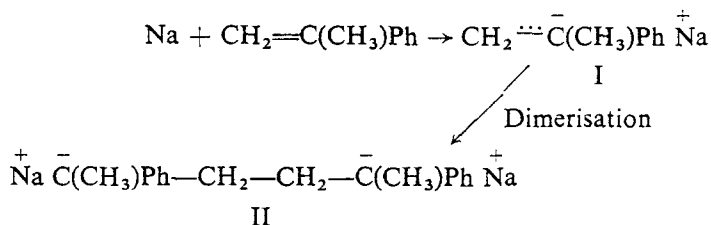
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**Abstract**—A method is described for preparing new polyalcohol regular copolymers which are of low molecular weight and which can possess a predetermined functionality and chain length. The procedure involves the reaction in tetrahydrofuran of a vinyl monomer with alkali metal in the presence of epichlorohydrin or a diepoxide. Examples are given of a number of copolymers prepared in this way, together with spectroscopic evidence for the proposed structures.

RECENTLY we described a method for synthesising regular copolymers by reacting certain vinyl or diene monomer solutions in tetrahydrofuran (THF) with alkali metal in the presence of calculated amounts of dihalides.<sup>(1)</sup> Under these conditions, polymers with the repeat unit  $[-M-R-M]-$  were produced, M being the monomer and R the ligand of the dihalide. The regularity of the structure was established by detailed NMR spectroscopy.<sup>(2)</sup>

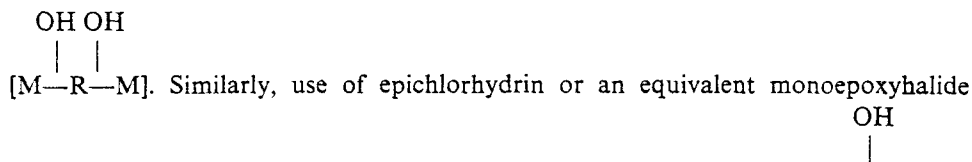
A similar procedure has been developed with epichlorohydrin and diepoxides wholly or partially replacing the dihalide, to produce polyalcohol copolymers with predetermined functionalities. The details of this technique are presented here.

When vinyl and diene monomers, such as styrene and butadiene, react with alkali metal in the presence of a good cation solvating solvent such as THF, a monomer radical anion is first formed which can then dimerise to form a dimer dianion. Thus for  $\alpha$ -methylstyrene and sodium



The dimer II may also be obtained by reaction of I with monomer to form a dimer radical anion which subsequently reacts with a further metal atom to form the dianion. By either route, one obtains the same dimer (II) containing a central tail to tail link so that the resonance stabilised benzylic anions are obtained at both ends.<sup>(3,4)</sup> Thus, with dihalides present in solution at a 1:2 molar ratio with monomer, a metathetical reaction with elimination of alkali halide takes place to give the regular copolymers described above.

The epoxide ring is also subject to nucleophilic attack, the nucleophile reacting additively to give an alcoholate. Indeed, Richards and Szwarc<sup>(5)</sup> have reacted polystyrene living polymers with ethylene oxide to give polystyrene telechelic diols, and further produced polystyrene-polyethylene oxide block copolymers by homopolymerising excess ethylene oxide on the polystyrene alcoholate ends. Thus it seems feasible that the generation of the dimer dianion of type II in the presence of a diepoxide at a monomer: diepoxide molar ratio of 2:1 would result in the formation of a polyalcohol regular copolymer containing two alcohol groups per repeat unit, i.e.



would generate a copolymer with one alcohol group per repeat unit  $[\text{M}-\text{R}-\text{M}]$ . Thus, by judicious choice of the relative proportions of epoxide, epichlorhydrin and dihalide in the reaction mixture whilst maintaining the overall molarity of the linking agents at one half that of the monomer, polyalcohols of a variety of functionalities may be prepared.

The molecular weight of the product can be controlled by adding calculated amounts of an appropriate alkyl monohalide to the reaction mixture. Being monofunctional, such additives act as chain stoppers rather than linking agents<sup>(6)</sup> and the number of moles of polymer chains formed should theoretically equal half the number of moles of monohalide added.

This communication describes some of the reactions carried out with styrene and  $\alpha$ -methylstyrene on diepoxides and epichlorhydrin.

## EXPERIMENTAL

### *Reaction temperature control*

The required reaction temperatures were maintained to  $\pm 1^\circ$  by using a heating or cooling bath sitting on a Jack-o-matic pneumatically operated stand controlled by a thermowatch detector, both supplied by Instruments for Industry and Research.

### *Infra-red spectroscopy*

Infra-red measurements were carried out on a Perkin-Elmer 337 grating spectrophotometer. Standard solutions of the polyols were prepared in carbon tetrachloride.

### *Nuclear magnetic resonance spectroscopy*

<sup>1</sup>H NMR spectra were obtained using a Perkin-Elmer R10 60 MHz spectrometer. Solutions in carbon disulphide or carbon tetrachloride were used and chemical shifts measured with respect to tetramethylsilane as internal standard. An associated Digiacc computer enabled accumulated spectra to be produced for more accurate analysis.

## MATERIALS

### *Monomers*

Styrene and  $\alpha$ -methylstyrene were stored over molecular sieves type 4A,  $\frac{1}{16}$  in. pellets (B.D.H.) for some days before filtering and standing over crushed calcium hydride overnight. The monomers were then vacuum distilled from further crushed calcium hydride immediately before use.

### *Epoxides*

The diepoxides were stored over calcium hydride overnight; hydroxyl groups present in some diepoxides, e.g. Araldite 750, could be neutralised. The materials were filtered immediately before addition to the reaction mixture. Epichlorhydrin was dried over crushed calcium hydride, and distilled immediately before use.

### *Alkyl halides*

The alkyl halides were stored over molecular sieves, filtered and fractionally distilled *in vacuo* from calcium hydride. The centre cut (about 70 per cent) was used in the reactions.

### *Metal*

Lithium metal (B.D.H.) in rod form was washed in petroleum ether and sliced into sections about 3–4 mm thick.

Sodium metal (B.D.H.) was washed with petroleum ether and pressed into wire before reacting.

### *Solvent*

Tetrahydrofuran was stored over molecular sieves, filtered, and allowed to stand for a few hours over freshly drawn sodium wire. It was then refluxed for 1 hr, distilled and stored over fresh sodium wire.

### *Polymerisation procedure*

The polymerisation procedures were very similar regardless of the monomer, alkali metal, or linking agents used. One example only of the method will therefore be described.

#### *Reaction of $\alpha$ -methylstyrene, lithium, epichlorhydrin and $\alpha,\omega$ -dibromodecane*

Purified THF (100 ml) was placed in a 250 ml, three-necked flask, cooled to 0° and nitrogen bubbled through with constant stirring. A two-fold excess of lithium metal was then added and the mixture stirred for about 15 min.  $\alpha$ -Methylstyrene (11.8 g, 0.1 mole), epichlorhydrin (2.31 g, 0.025 mole), and dibromodecane (7.5 g, 0.025 mole) were then introduced, the nitrogen flow was discontinued and the flask sealed. After an induction period of about 30 min, the lithium surface became yellow and the reaction started. The reaction was continued for about 5 hr when the lithium surface took on a silvery aspect. Excess lithium was removed, and the bulk of the solution was reduced on a rotary film evaporator. The remaining solution was then slowly added to about 1.5 l. of acidified methanol with constant stirring. The brittle white solid thus formed was dried for 24 hr at room temperature in a vacuum oven.

### *Viscosities and molecular weights*

The specific viscosities of 1 per cent w/v solutions of the polymers in tetrahydrofuran were determined at 25° to give a measure of the chain length.

Molecular weights of the low molecular weight polymers were determined on a Mechrolab Vapour Pressure Osmometer using acetone as solvent.

## RESULTS

The reactions were carried out at temperatures between 0° and +30° using lithium or sodium as initiator. In all cases, the reaction proceeded smoothly after an induction period of about 30 min when the onset of reaction was indicated by a marked change in the appearance of the alkali metal. Its surface changed from a dull colour to a bright, shiny aspect; it was therefore assumed that the induction was due to the slow removal of the surface oxide layer from the metal.

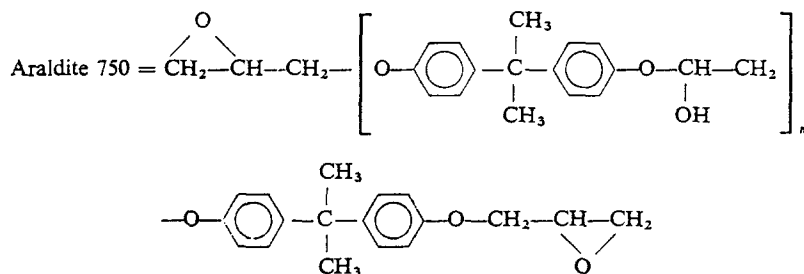
The main preparative details and the analytical data of representative examples of polymers prepared in this way are listed in Table 1. All the products were hard white solids. The theoretical aliphatic to aromatic hydrogen ratios listed in Table 1 are calculated assuming that the hydroxyl hydrogen aromatic absorption is located in the aliphatic hydrogen absorption range (6 to 10 $\tau$ ). The experimental ratios were assessed by automatic integration of the peak areas of accumulated spectra.

TABLE 1

Run No.	Monomer	Alkali metal	Epoxide (mole %)	Halide (mole %)	$\eta$ sp	Aliphatic:Aromatic <sup>1</sup> H ratios	
						Theoretical	Obtained
1	$\alpha$ -methylstyrene	Li	100 ECH	0	0.078	1.60	1.50
2	$\alpha$ -methylstyrene	Li	75 ECH	25(CH <sub>2</sub> ) <sub>4</sub> Br <sub>2</sub>	0.092	1.65	1.68
3	$\alpha$ -methylstyrene	Li	50 ECH	50(CH <sub>2</sub> ) <sub>4</sub> Br <sub>2</sub>	0.108	1.70	1.62
4	$\alpha$ -methylstyrene	Li	25 ECH	75(CH <sub>2</sub> ) <sub>4</sub> Br <sub>2</sub>	0.110	1.75	1.73
5	$\alpha$ -methylstyrene	Li	0 ECH	100(CH <sub>2</sub> ) <sub>4</sub> Br <sub>2</sub>	0.119	1.80	1.80
6	$\alpha$ -methylstyrene	Li	75 ECH	25(CH <sub>2</sub> ) <sub>4</sub> Br <sub>2</sub>	0.120	1.65	1.62
7	$\alpha$ -methylstyrene	Na	75 ECH	25(CH <sub>2</sub> ) <sub>4</sub> Br <sub>2</sub>	0.060	1.65	1.60
1	$\alpha$ -methylstyrene	Li	100 ECH	0	0.078	1.60	1.50
8	$\alpha$ -methylstyrene	Li	75 ECH	25(CH <sub>2</sub> ) <sub>10</sub> Br <sub>2</sub>	0.068	1.95	2.13
9	$\alpha$ -methylstyrene	Li	50 ECH	50(CH <sub>2</sub> ) <sub>10</sub> Br <sub>2</sub>	0.080	2.30	2.40
10	$\alpha$ -methylstyrene	Li	25 ECH	75(CH <sub>2</sub> ) <sub>10</sub> Br <sub>2</sub>	0.111	2.65	2.50
11	$\alpha$ -methylstyrene	Li	0 ECH	100(CH <sub>2</sub> ) <sub>10</sub> Br <sub>2</sub>	0.218	3.0	2.90
12	$\alpha$ -methylstyrene	Li	67 ECH	33C <sub>4</sub> H <sub>9</sub> Br	—	1.97	1.90
13	Styrene	Li	67 ECH	33C <sub>4</sub> H <sub>9</sub> Br	—	1.60	1.40
14	Styrene	Li	50 ECH	50(CH <sub>2</sub> ) <sub>3</sub> Br <sub>2</sub>	0.074	1.20	1.20
15	Styrene	Li	50 ECH	50(CH <sub>2</sub> ) <sub>6</sub> Br <sub>2</sub>	0.066	1.50	1.45
16	$\alpha$ -methylstyrene	Li	100 DEPP	0	—	1.55	1.55
17	$\alpha$ -methylstyrene	Li	100 Araldite 750	0	—	1.40	1.40

ECH = Epichlorhydrin.

DEPP = *pp'*-diglycidyl ether of 2,2'-diphenylpropane.



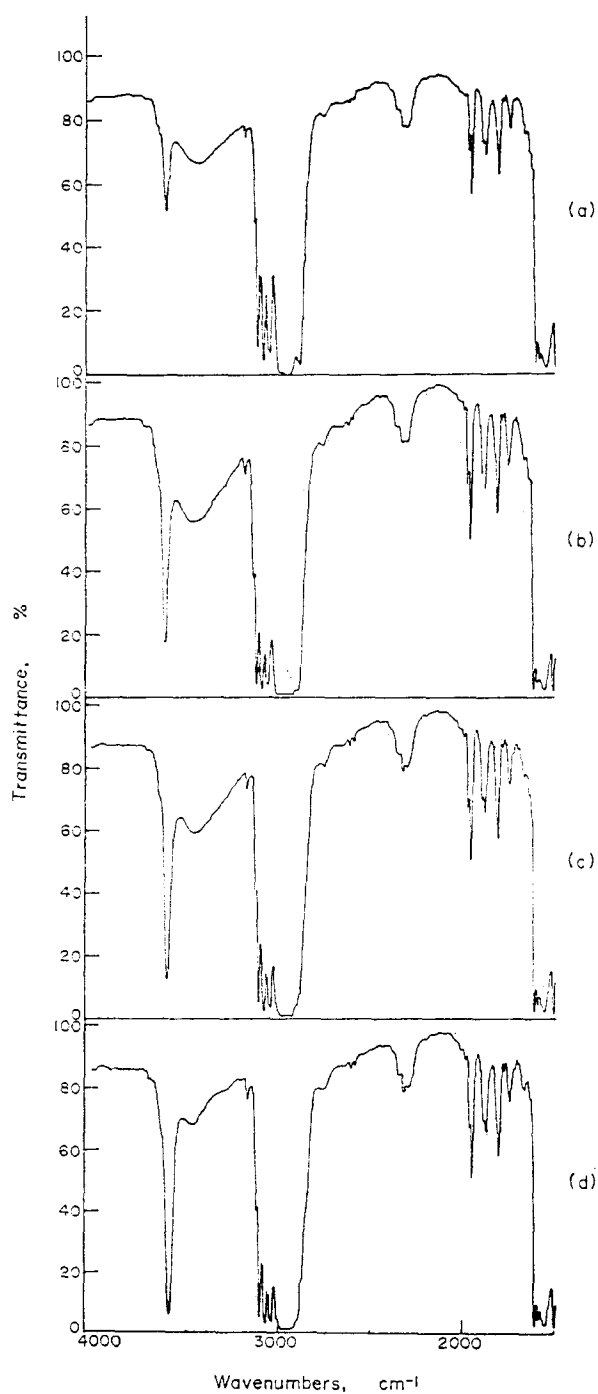


FIG. 1. Infra-red spectra of polyalcohols prepared from  $\alpha$ -methylstyrene, epichlorohydrin, and  $\alpha$ - $\omega$ -dibromobutane (a) 25% ECH, 75%  $(\text{CH}_2)_4\text{Br}_2$ ; (b) 50% ECH, 50%  $(\text{CH}_2)_4\text{Br}_2$ ; (c) 75% ECH, 25%  $(\text{CH}_2)_4\text{Br}_2$ ; (d) 100% ECH, 0%  $(\text{CH}_2)_4\text{Br}_2$ .

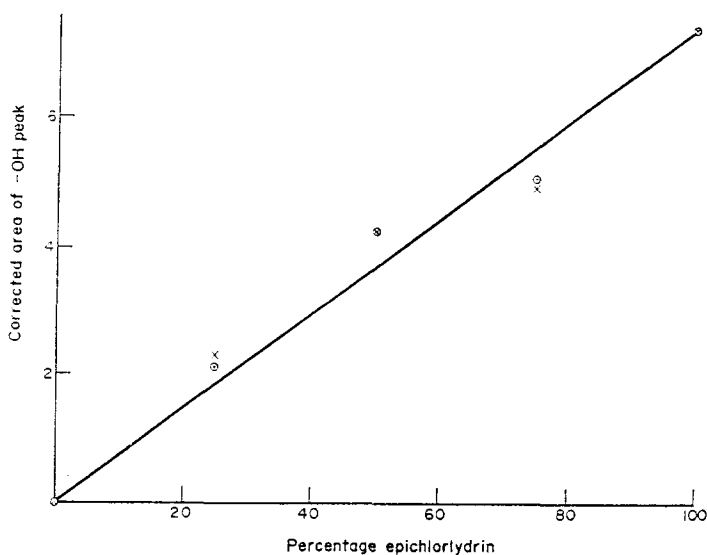


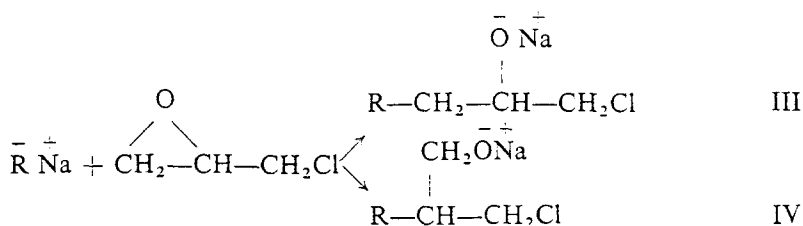
FIG. 2. Corrected areas of non-bonded hydroxyl peak at  $3580\text{ cm}^{-1}$  plotted against epichlorhydrin content. ○ "Butane" copolymer. × "Decane" copolymer.

Infra-red spectra in the range  $1500\text{--}3500\text{ cm}^{-1}$  for a series of  $\alpha$ -methylstyrene copolymers, where the molar ratios of epichlorhydrin and  $\alpha,\omega$ -dibromobutane are varied, are given in Fig. 1. The linearity between the non-bonded hydroxyl absorption at  $3580\text{ cm}^{-1}$  and the epichlorhydrin content of the reaction mixture is illustrated in Fig. 2.

### DISCUSSION

The general agreement shown in Table 1 between the observed and predicted values for aliphatic to aromatic hydrogen ratios indicates that the reaction proceeds via the formation of a dimer dianion which subsequently reacts additively with the epoxide or metathetically with the alkyl halide. This view is supported by the formation of model compounds with structures of the type  $\text{HO}(\text{CH}_2)_2\text{M}-\text{M}(\text{CH}_2)_2\text{OH}$  when monoepoxides such as ethylene oxide are used as terminating agents.<sup>(7)</sup> Further evidence is given by i.r. spectra such as the series shown in Fig. 1. The sharp absorption peak at  $3580\text{ cm}^{-1}$  is due to free hydroxyl stretching whereas the broad band centred at  $3460\text{ cm}^{-1}$  is the hydrogen bonded hydroxyl stretch. The hydrogen bonded component could be due to intra-molecular association of the polyalcohol or at least partially due to the presence of traces of methanol still in the polymer. However, the relative areas of the two peaks indicate that 90–95 per cent of the hydroxyls are in the unbonded form.<sup>(8)</sup> In Fig. 2 the peak areas at  $3580\text{ cm}^{-1}$  are plotted against the epichlorhydrin content for two copolymer series:  $\alpha$ -methylstyrene, epichlorhydrin,  $\alpha,\omega$ -dibromobutane, and  $\alpha$ -methylstyrene, epichlorhydrin,  $\alpha,\omega$ -dibromodecane. The peak areas of the latter copolymers were corrected to allow for increase in average molecular weight of the repeat unit with decamethylene content. It is seen that the two series are in very good agreement with each other and that a linear relationship exists between the hydroxyl content of the copolymers and the amount of epichlorhydrin used.

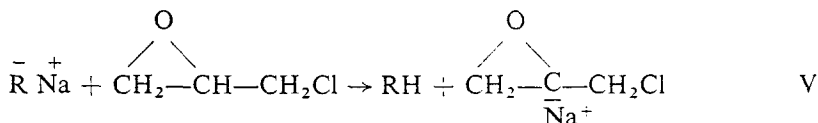
The epoxide group can react additively in two ways. For example, a nucleophilic reagent ( $\text{R}^-\text{Na}^+$ ) may attack epichlorhydrin to produce a primary or secondary alcoholate, thus:—



It is expected that III would predominate as it has been shown that nucleophilic additive attack on epoxides occurs almost exclusively at the terminal carbon.<sup>(9, 10)</sup>

Both entities can eliminate sodium chloride to produce the epoxide

$\text{R}-\text{CH}_2-\text{CH}-\text{CH}_2$  from III and the  $\alpha$ -substituted trimethylene oxide  $\text{R}-\text{CH}-\text{O}-\text{CH}_2-\text{CH}_2$  from IV. Of course, the epoxide formed from III is identical to that formed if the carbon-chloride bond of epichlorhydrin were attacked first, and it can continue in the polymerisation process. No spectroscopic evidence has so far been obtained for the presence of trimethylene oxide groups in the product. However, the low specific viscosities given by the polymers and their decrease with increase of epichlorhydrin content indicates that some form of chain stopping or chain transfer process does exist and that it is related to the presence of epoxide. Such a reaction could well be that of chain transfer by proton abstraction of the tertiary hydrogen attached to the epoxide ring, viz:



A similar postulate was made by Richards and Szwarc<sup>(5)</sup> who were unable to prepare block copolymers of styrene with propylene oxide or styrene oxide, although styrene-ethylene oxide block copolymers had been readily synthesised. Further support for this view is given by the observation that polyalcohols prepared using lithium metal are invariably of higher molecular weight than those prepared with sodium under identical experimental conditions (Table 1, runs 6 and 7). The sodium alkyls, being stronger bases, abstract hydrogen more readily than the weaker lithium compounds. Experiments are in hand with  $\beta$ -methyl-epichlorhydrin to determine whether substitution of the tertiary hydrogen by a methyl group results in copolymers with longer chains.

Experiments were conducted to produce oligomers of predetermined average molecular weight and hydroxyl functionality by adding small amounts of monohalide to the reaction mixture. Calculations of the quantities required were based on the admittedly incorrect assumption that the sole chain stopping reaction occurring was that involving the monohalide. Despite this limitation, oligomers were produced

having molecular weights reasonably close to those calculated. Thus for  $\alpha$ -methylstyrene as monomer (Table 1, run 12) a molecular weight of 1690 was obtained (calculated 1522) and for styrene (run 13) an experimental value of 850 was obtained (calculated 1326). Both these materials were used in the preparation of new polyurethanes which are currently being evaluated.

A number of experiments were performed with diepoxides as linking agents. Most of the diepoxides were not well characterised commercial materials and so are not listed in Table 1, but, as with epichlorhydrin, hard white solids were obtained when vinyl monomers were used. One experiment using *p,p'*-diglycidyl ether of 2,2'-diphenylpropane (DEPP) did, however, give a solid which on  $^1\text{H}$  NMR analysis gave excellent agreement with theory (run 14). It appears therefore that diepoxides can be used in this process and an example of the use of one of the better characterised commercial diepoxides, Araldite 750, is given in Table 1 (run 17).

Similar work is continuing using dienes such as butadiene as monomers and will be reported in a later communication.

*Acknowledgements*—We thank Mrs. P. Fuller for carrying out the  $^1\text{H}$  NMR measurements.

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**Résumé**—On décrit une méthode pour préparer de nouveaux copolymères réguliers de polyalcool, de faibles masses moléculaires, qui possèdent une fonctionnalité et une longueur de chaîne prédéterminées. Le procédé comporte la réaction, en milieu tétrahydrofurane, d'un monomère vinylique avec un métal alcalin en présence d'epichlorhydrine ou d'un diépoxyde. On donne les exemples de nombreux copolymères préparés selon ce procédé, accompagnés de la preuve spectroscopique qu'ils possèdent bien la structure proposée.

**Sommario**—Si descrive un metodo per la preparazione di nuovi copolimeri regolari polialcolici che hanno un basso peso molecolare e che possono possedere una determinata funzionalità e lunghezza di catena. Il procedimento comprende la reazione, in tetraidrofurano, di un monomero vinilico con un metallo alcalino in presenza di epichloridrina oppure di un diepossido. Si forniscono esempi di un certo numero di copolimeri preparati in questo modo, assieme alla prova spettroscopica che essi hanno la struttura prevista.

**Zusammenfassung**—Es wird eine Methode zur Herstellung von neuen regelmäßigen Polyalkohol Copolymeren beschrieben, die ein niedriges Molekulargewicht besitzen und eine vorausbestimmte Funktionalität und Kettenlänge haben können. Das Verfahren besteht in der Reaktion eines Vinylmonomeren mit Alkalimetall in Tetrahydrofuran bei Gegenwart von Epichlorhydrin oder einem Diepoxid. Für eine Anzahl von derart hergestellten Copolymeren werden Beispiele angeführt, zusammen mit spektroskopischen Befunden, die die vorgeschlagene Struktur beweisen.