Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Epoxidation of Alkyllithium Polybutadienes

Henry S. Makowski[a]; Merrill Lynn[a]; Don H. Rotenberg[a]
[a] Esso Research & Engineering Co. Linden, New Jersey

To cite this Article Makowski, Henry S. , Lynn, Merrill and Rotenberg, Don H.(1970) 'Epoxidation of Alkyllithium Polybutadienes', Journal of Macromolecular Science, Part A, 4: 7, 1563 — 1597

To link to this Article: DOI: 10.1080/00222337008069370

URL: http://dx.doi.org/10.1080/00222337008069370

J. MACROMOL. SCI.–CHEM., A4(7), pp. 1563-1597, November, 1970

Epoxidation of Alkyllithium Polybutadienes

HENRY S. MAKOWSKI, MERRILL LYNN, and DON H. ROTENBERG
Esso Research & Engineering Co.
Linden, New Jersey 07036

SUMMARY

Epoxidations with peracetic acid were effected on a series of alkyllithium and sodium polybutadienes, and the properties of the epoxy resins were compared. The alkyllithium and sodium polybutadienes differed in microstructure and molecular weight distribution. The alkyllithium polybutadienes were more readily epoxidized, and epoxidation resulted in dramatically lower viscosity increases with increasing epoxy contents. Epoxidized alkyllithium polybutadienes varying in molecular weight and epoxy content were shown to be compatible, efficient, and permanent plasticizer-stabilizers for polyvinyl chloride.

INTRODUCTION

A substantial amount of information has been published on the epoxidation of low molecular weight liquid polybutadienes [1-12]. Most of the work, however, has been concerned with sodium-initiated polybutadienes which contain largely vinyl (Type I) unsaturation [13] and, in addition, are highly viscous.

Alkyllithium polymerization of butadiene under appropriate conditions results in polymers which are low in viscosity and high in 1,4-addition (Type II unsaturation) [14-16]. The resultant unsaturation is more reactive to epoxidation than Type I unsaturation. Also the molecular weights of alkyllithium polybutadienes can be easily and precisely varied over a very wide molecular weight range. These desirable factors prompted the investigation of the epoxidation of alkyllithium polybutadienes and the properties of the epoxidized resins.

EXPERIMENTAL

Starting Materials

Butyllithium polybutadienes were prepared according to procedures described previously [14-16].

Sodium-initiated polybutadienes varying in number-average molecular weight and bulk viscosity were obtained by the acetone extraction of a commercial polybutadiene (Buton 150, Lot D-511-C, Enjay Chemical Co). A mixture of polybutadiene and acetone (1.0 to 8.0 ml/g resin) was thoroughly agitated for 2 hr and then permitted to settle. The acetone layer was carefully separated, and the acetone stripped off under reduced pressure. The residual polybutadiene was kept at 100°C for 2 hr at 2 mm Hg to insure solvent removal. The properties of the sodium-initiated polybutadienes are given in Table 1, and the bulk viscosity-$\overline{M}_n$ relationship is illustrated in Fig. 1.

Dowex Resin 50 W-X8, ionic form, was obtained from the J. T. Baker Co. and conditioned according to prescribed procedures [17].

50% Hydrogen peroxide (Albone 50) was obtained from Electrochemicals Department, E. I. du Pont de Nemours & Co., Inc.

Analytical Methods

Kinematic viscosities were determined at 25°C according to ASTM 445.

Number-average molecular weights ($\overline{M}_n$) were determined with a Mechrolab vapor-pressure osmometer.

Polybutadiene microstructures were calculated from the peaks of maximal absorption appearing around 11.0 μ (Type I unsaturation), 10.4μ (Type II trans unsaturation), and 13.5 μ (Type II cis unsaturation) as described previously [14].

The compositions of butadiene–styrene copolymers were determined via NMR measurements.

Oxirane oxygen was determined by a slight modification of the procedure of Durbetaki [18]. Excess HBr in acetic acid was added to the epoxidized polymer. After 10 min the excess HBr was titrated with standard sodium acetate solution to a crystal violet end-point.

Table 1. Properties of Sodium Initiated Polybutadienes

Properties												
Kinematic viscosity (25°C), St	2.47	3.4	4.99	5.96	6.1	7.0	10.1	16.0	15.2	45.0	[a]	1.28
Number av MW, $\bar{M}_n$	630	720	780	790	980	920	1030	1150	1070	1300	1680	605
Unsaturation												
Type I, %	71.1	–	71	71.8	–	–	–	71.1	–	–	72.8	–
Type II, cis, %	6.3	–	8	7.2	–	–	–	8.1	–	–	6.9	–
Type II, trans, %	22.6	–	21	21.0	–	–	–	20.8	–	–	20.3	–

[a] Base polymer for acetone extractions.

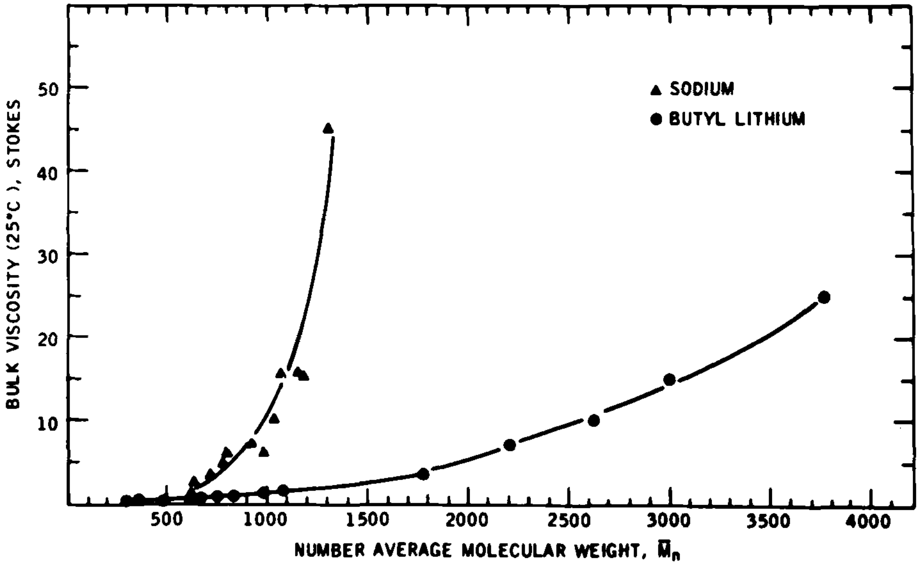

Fig. 1. Viscosity-$\bar{M}_n$ relationships for sodium-initiated and butyllithium-initiated polybutadienes.

The total oxygen content of the epoxidized polymers was determined via neutron activation.

The compositions of aqueous peracetic acid were determined according to procedures supplied by the FMC Corporation [19].

Epoxidation of Sodium Polybutadienes with in situ Peracetic Acid

(a) Unsaturation Consumption. A series of 4 epoxidations on a polybutadiene of $\bar{M}_n$ 780 was effected under rather arbitrary conditions. For every mole of double bond to be epoxidized the following proportions were used:

Hydrogen peroxide (50%)	1.1	moles
Acetic acid	0.55	mole
Dowex Resin 50W-X8	180	g
Benzene	2500	ml

The benzene diluent, acetic acid, Dowex Resin, and polybutadiene were charged to a 4-necked round-bottom flask fitted with a stirrer, thermometer, reflux condenser, and dropping funnel. The hydrogen peroxide was added at room temperature with agitation over a period of about 5 min. No exotherm was noted. The temperature of the reaction mixture was raised to 60°C and maintained at 60°C for 2 hr. At the end of this time an equal volume of water was added. The aqueous layer and Dowex resin were separated via a separatory funnel. The benzene solution was washed twice with an equal volume of saturated sodium bicarbonate solution. The benzene solution was dried over magnesium sulfate, filtered, and stripped under reduced pressure (0.2 mm Hg). At the end of the stripping, the temperature was raised to 75°C and kept there for 1 hr. The resin was polish filtered through diatomaceous earth.

The resins were analyzed for epoxy content, number-average molecular weight, kinematic viscosity, and type residual unsaturation. Results are given in Table 2.

(b) Molecular Weight Variations. A series of 4 epoxidations was effected on 3 polybutadienes of $\bar{M}_n$ 630, 790, and 1150.

A 12-liter, 4-neck round-bottom flask was fitted with a reflux condenser, thermowell, stirrer, and dropping funnel. The flask was charged with polybutadiene, conditioned Dowex resin [17], and benzene according to the following proportions:

H_2O_2: 1.1 moles/mole of double bond to be epoxidized.

Benzene: 550 ml/mole H_2O_2.

Conditioned Dowex Resin: enough to provide 0.5 mole acetic acid/mole of H_2O_2.

The hydrogen peroxide was added over a 1-hr period to the well stirred and cooled (40-55°C) reaction mixture. The reaction mixture was then heated at 60°C for 2 hr. Chipped ice was added to quench the reaction and the benzene layer was separated. The benzene solution was washed twice with an equal volume of water and once with saturated sodium bicarbonate solution. Difficulty was encountered in the separation of the washes. The benzene solution was dried over anhydrous $MgSO_4$, filtered, and vacuum stripped. The residual epoxy polybutadiene was kept at 100°C for 2 hr at 2 mm Hg to insure solvent removal.

This procedure was satisfactory for achieving the desired epoxy levels and was quite reproducible. Product recoveries were low (60-77%) due to failure of aqueous and benzene phases to separate sharply during washing.

Yields and product properties are given in Table 3.

Table 2. In Situ Epoxidation of Sodium Initiated Polybutadiene, $\overline{M}_n$ 780

	Starting PBD				
Polybutadiene, g	–	54.0	54.0	54.0	54.0
H_2O_2, moles	–	0.11	0.22	0.276	0.33
Yield, g	–	32.5	49.0	41.0	53.0
Product properties					
No. av MW, $\overline{M}_n$	780	870	870	910	860
Kinematic viscosity (25°C), St	4.99	15.6	37.0	65.3	–
Oxirane oxygen, mequiv./g	–	1.90	3.44	4.13	4.41
Epoxy equivalent	–	526	290	242	226
Relative unsaturation					
Type I	71	–	71	–	54
Type II, trans	21	–	9	–	4
Type II, cis	8	–	6	–	6

Epoxidation of Alkyllithium Polymers with Aqueous Peracetic Acid

Three alkyllithium polymers were used in these studies and had the properties shown in Table 4.

A butadiene–styrene block copolymer was prepared as described previously for polybutadiene [14-16]. Butadiene (8.0 moles) was polymerized with n-butyllithium (1.0 mole) in toluene and then styrene (2.0 moles) added thereto.

Aqueous peracetic acid was generated according to the procedure provided by the FMC Corporation [19]. Since it equilibrates on standing it was refrigerated upon generation and used within a few days of generation. Although higher strength aqueous peracetic acid solutions are easily obtained, the peracetic acid generator was operated at throughputs that produced the following typical composition:

Peracetic acid = 27 wt%
Acetic acid = 20 wt%
H_2O_2 = 4.5 wt%
H_2O = 48.5 wt%

This typical composition corresponds to an equivalent acetic acid/H_2O_2 ratio of about 1.4 whereas the in situ procedure operates at a ratio of about 0.5. Thus the aqueous peracetic acid used in these studies contains a substantially higher amount of acetic acid. A composition of 40% peracetic acid, 15% acetic acid, and a trace of H_2O_2 is readily obtained [19] but was not prepared for these studies. At this composition the equivalent acetic acid/H_2O_2 ratio is about 0.7.

A typical equilibrium peracetic acid [20] contains about 35-40% peracetic, 40-50% acetic acid, 12-14% water, and 3-6% H_2O_2 besides about 1% sulfuric acid.

(a) General Epoxidation Procedure. A toluene solution of the polymer was charged to a 2-liter 4-necked round-bottom flask fitted with a stirrer, a condenser, a thermometer, and a dropping funnel. The solution was brought up to the desired temperature (60°C) and peracetic acid solution added incrementally over a 2-hr period with good agitation. The reaction mixture was stirred for an additional period of time at this temperature. The reaction mixture was quenched with cold water. The toluene solution was washed to neutrality with water and finally with saturated sodium

Table 3. In Situ Epoxidation of Sodium Initiated Polybutadienes

No. av MW of starting polybutadiene	630	630	630	630	790	790	790	790
Epoxidation								
Polybutadiene, g	1760	1760	1760	1760	1760	1760	1760	1760
Conditioned Dowex resin, g	1032	1150	1262	1376	1030	1150	1262	1376
Acetic acid, moles	3.23	3.60	3.95	4.32	3.23	3.60	3.95	4.32
Hydrogen peroxide, moles	6.47	7.19	7.90	8.60	6.47	7.19	7.90	8.60
Benzene, liters	2.94	3.27	3.59	4.32	2.94	3.27	3.59	4.33
Recovered product, g	1210	1220	1058	1125	1358	1313	1252	1253
Product properties								
Oxirane oxygen, mequiv./g	3.35	3.52	3.88	4.00	3.19	3.45	3.64	4.00
Epoxy equiv.	298	284	258	250	313	290	274	250
No. av MW, $\overline{M}_n$	640	640	700	690	880	910	890	930
Kinematic viscosity (25°C), St	8.7	10.2	17.9	21.4	36.1	48.9	35.7	71.6

No. av MW of starting polybutadiene	1150	1150	1150	1150	1150	1150	1150	1150
Epoxidation								
Polybutadiene, g	1090	1090	1090	872	1760	1760	1760	1760
Conditioned Dowex ressin, g	231	306	406	367	1032	1150	1262	1370
Acetic acid, moles	0.825	1.10	1.375	1.40	3.23	3.60	3.95	4.32
Hydrogen peroxide, moles	1.65	2.20	2.75	2.64	6.47	7.19	7.90	8.60
Benzene, liters	3.75	5.0	6.25	6.0	2.94	3.27	3.59	4.32
Recovered product, g	912	957	993	791	1114	1063	1266	1165
Product properties								
Oxirane oxygen, mequiv./g	1.46	1.87	2.34	2.71	3.13	3.59	3.68	3.93
Epoxy equiv.	685	535	427	369	320	279	272	254
No. av MW, $\overline{M}_n$	1210	1200	1260	1170	1300	1180	1260	1230
Kinematic viscosity (25°C), St	26.1	32.0	57.5	71.7	148	275	414	574

Table 4. Properties of Alkyllithium Polymers

	Polybutadiene	Polybutadiene	Styrene–butadiene copolymer
Mole % styrene	0	0	21
No. av MW, $\bar{M}_n$	680	2350	750
Kinematic viscosity (25°C),	0.48	8.36	6.59
Unsaturation			
% Type I	17	13	17
% Type II	83	87	83

bicarbonate. The toluene solution was dried with anhydrous $MgSO_4$ and stripped under vacuum. The product was kept at 100°C for 2 hr at 2-4 mm Hg. The product was treated with Celite and anhydrous $MgSO_4$ and filtered hot under nitrogen through a heated scintered glass funnel.

(b) Effect of Reaction Time. In order to establish suitable and reproducible conditions for epoxidation with aqueous peracetic acid a series of epoxidation runs on polybutadiene, $\bar{M}_n$ 680, in toluene solution were made in which the peracetic acid concentration (3 levels) and the reaction time after peracetic acid addition (4 levels) were varied.

Results and product properties are given in Table 5. The data show that, for a peracetic acid addition period of 2 hr, no increase in epoxy content is obtained at additional reaction time in excess of 30 min.

(c) Effect of Peracetic Acid Concentration. All runs were made as described above. After total peracetic acid addition the reaction mixture was stirred 60 min and then worked up.

Data for polybutadiene $\bar{M}_n$ 680, are given in Table 6, those for the butadiene–styrene copolymer are given in Table 7 and those for polybutadiene, $\bar{M}_n$ 2350, are given in Table 8.

(d) Analysis of Data. Oxirane oxygen was determined directly by HBr titration, and total oxygen was obtained by neutron activation. The difference between total oxygen and oxirane oxygen was assumed to be due solely to hydroxy acetate resulting from epoxide reaction with acetic acid.

Table 5. Epoxidation of Alkyllithium Polybutadiene ($\bar{M}_n$ 680) with Aqueous Peracetic Acid. Effect of Reaction Time

Desired epoxy equiv.[a]	220	220	220	220	200	200	200	200	180	180	180	180
Polybutadiene, g	136.8	136.8	136.8	136.8	136.8	136.8	136.8	136.8	136.8	136.8	136.8	136.8
Toluene, g	663	663	663	663	663	663	663	663	663	663	663	663
Peracetic acid solution, g	207.5	207.5	207.5	207.5	229	229	229	229	275.5	275.5	275.5	275.5
Peracetic acid, g.	56.0	56.0	56.0	56.0	62.1	62.1	62.1	62.1	69.8	69.8	69.8	69.8
Additional stirring tim, min[b]	30	60	120	240	30	60	120	240	30	60	120	240
Yield, g	144.4	132.1	131.6	129.6	124.1	140.2	146.7	136.0	127.1	140.4	133.3	134.0
Product properties												
Kinematic viscosity (25° C), St	1.43	1.36	1.39	1.48	1.76	1.67	1.73	1.85	2.06	2.06	2.23	2.35
Oxirane oxygen, mequiv./g	3.94	3.82	3.62	3.95	4.40	4.26	4.31	4.44	4.63	4.64	4.74	4.76
Epoxy equiv.	254	262	276	253	227	235	232	225	216	213	211	210

[a] Based on use of 10% excess of peracetic acid.

[b] After total peracetic acid addition.

Table 6. Epoxidation of Alkyllithium Polybutadiene (M_n 780) with Aqueous Peracetic Acid. Effect of Peracetic Acid Concentration

Starting resin, g	136.8	136.8	136.8	136.8	136.8	136.8	136.8	136.8	136.8	136.8	136.8
Toluene, g	663	663	663	663	663	663	663	663	663	663	663
Peracetic acid, g	56.0	62.1	67.0	69.8	75.2	82.1	95.8	95.8	109.4	123.1	136.8
Peracetic acid/resin, g	0.41	0.45	0.49	0.51	0.55	0.60	0.70	0.70	0.80	0.90	1.00
Moles peracetic acid/ mole unsaturation	0.318	0.348	0.379	0.395	0.426	0.465	0.542	0.542	0.618	0.694	0.777
Yield, g	132.1	140.2	139.5	140.4	141.2	144.5	143.8	144.0	141.2	129.7	150.3
Product properties											
Kinematic viscosity (25°C), St	1.36	1.67	2.12	2.06	2.66	3.45	5.41	4.81	8.00	13.99	20.98
Oxirane oxygen, mequiv./g	3.82	4.26	4.77	4.64	5.06	5.27	5.58	5.74	5.73	5.86	5.85

Epoxy equivalent	262	235	210	213	198	190	180	174	175	171	171
No. av MW, $\overline{M}_n$	729	737	750	752	683	770	761	701	774	797	796
Oxirane oxygen, wt%	6.05	6.75	7.63	7.45	8.10	8.40	9.00	9.18	9.25	9.50	9.50
Total oxygen, wt%	6.62	8.31	9.46	9.45	10.1	11.4	12.5	12.5	15.9	16.9	15.4
Product composition, mole%											
Unsaturation	75.3	70.1	66.4	66.4	63.6	60.1	55.9	55.9	47.1	44.0	47.8
Oxirane	23.9	27.8	31.4	30.7	33.5	35.5	38.8	39.5	42.5	44.3	43.0
Hydroxy acetate	0.8	2.1	2.5	2.8	2.8	4.2	5.0	4.8	10.2	11.5	8.9
Conv. of peracetic acid, %											
To oxirane	75.3	79.8	82.8	77.8	78.6	76.4	71.6	72.9	68.8	63.4	55.4
To hydroxy acetate	2.5	6.0	6.6	7.1	6.6	9.0	9.2	8.9	16.5	16.6	11.5
Total	77.8	85.8	89.4	84.9	85.2	85.4	80.8	81.8	85.3	80.0	66.9

Table 7. Epoxidation of Alkyllithium Butadiene–Styrene Copolymer (21% Styrene, $\overline{M}_n$ 750) with Aqueous Peracetic Acid. Effect of Peracetic Acid Concentration

Starting resin, g	144.8	144.8	144.8	144.8	144.8	144.8	144.8	144.8	144.8	144.8	144.8
Toluene, g	655	655	655	655	655	655	655	655	655	655	655
Peracetic acid, g	59.4	65.7	73.8	86.9	101.4	115.8	130.3	144.8	159.3	173.8	188.2
Peracetic acid, g/resin, g	0.41	0.45	0.51	0.60	0.70	0.80	0.90	1.00	1.10	1.20	1.30
Moles peracetic acid/ mole unsaturation	0.477	0.524	0.594	0.698	0.815	–	1.048	1.165	1.281	1.397	1.514
Yield, g	142.8	142.3	147.8	132.6	120.3	140.4	130.8	122.5	106.2	109.2	91.8
Product properties											
Kinematic viscosity (25°C), St	24.4	35.3	48.0	117.5	361.7	–	–	–	–	–	–
Oxirane oxygen, mequiv./g	3.49	3.93	4.07	4.43	4.13	4.03	3.67	2.97	3.14	2.85	2.65

Epoxy equivalent	286	254	246	226	242	248	277	337	317	351	377
No. av MW, $\overline{M}_n$	877	846	849	836	862	—	—	834	906	1005	955
Oxirane oxygen, wt%	5.65	6.25	6.45	7.05	6.60	6.40	5.75	4.75	5.00	4.57	4.25
Total oxygen, wt%	7.38	8.36	9.03	10.9	12.9	—	13.5	12.2	10.5	11.7	10.6
Product composition, mole %[a]											
Unsaturation	62.5	57.8	54.5	46.9	42.6	—	44.1	52.1	56.1	53.7	58.8
Oxirane	33.9	38.3	39.9	45.0	43.9	—	38.7	31.0	31.9	30.1	27.4
Hydroxy acetate	3.5	4.3	5.3	8.2	13.9	—	17.2	16.5	11.7	15.8	13.6
Conversion of peracetic acid, %											
To oxirane	71.1	73.1	67.2	64.5	53.9	—	36.9	26.6	24.9	21.5	18.1
To hydroxy acetate	7.3	8.2	8.9	11.7	17.1	—	16.4	14.2	9.1	11.3	9.0
Total	78.4	81.3	76.1	76.2	71.0	—	53.3	40.8	34.0	32.8	27.1

[a] Excluding styrene portion.

Table 8. Epoxidation of Alkyllithium Polybutadiene ($\bar{M}_n$ 2350) with Aqueous Peracetic Acid. Effect of Peracetic Acid Concentration

Starting resin, g	1088			
Toluene, g	5300			
Peracetic acid, g	762	598	446	533
Peracidic acid, g/resin, g	0.7	0.55	0.41	0.49
Moles peracetic acid/mole unsaturation	0.512	0.402	0.300	0.358
Yield of product, g	1044	987	965	1066
Product properties				
Kinematic viscosity (77°F), St	294	114	48.1	71.3
No. av MW, $\bar{M}_n$	2710	2580	2220	2400
Oxirane oxygen, mequiv./g	5.78	5.35	4.41	4.90
Epoxy equivalent	173	187	227	204
Total oxygen, wt%	15.1	11.40	8.09	9.83
Oxirane oxygen, wt%	9.25	8.56	7.06	7.84
Product composition, mole%				
Unsaturation	49.4	62.2	72.0	66.9
Oxirane	39.3	34.3	26.9	30.6
Hydroxy acetate	8.29	3.78	1.28	2.56
Conversion of peracetic acid, %				
To oxirane	76.8	85.3	85.5	89.7
To hydroxy acetate	16.2	9.4	7.2	4.2
Total	93.0	94.7	92.7	93.9

The number of double bonds per gram of resin for each of the three polymers studied was calculated from the composition and molecular weight or the resin. Since a butyl group, derived from the butyllithium initiator, is attached to each chain, this was taken into account in each calculation. The calculated values are:

Polymer	Double bonds/g resin
Polybutadiene, $\overline{M}_n$ 680	0.017
Polybutadiene, $\overline{M}_n$2350	0.018
Butadiene–styrene copolymer	0.0113

Unsaturation in the epoxidized resins was not determined directly. The wt% hydrocarbon in the epoxidized resin was calculated from the expression (100-wt% oxirane - wt% hydroxy acetate = wt% hydrocarbon). Initial unsaturation of the polymer was then calculated from the expression (double bonds/g resin) X (wt% hydrocarbon in epoxidized resin) = (moles unsaturation/100 g resin). The unsaturation in the epoxidized resin then was calculated from the expression (moles initial unsaturation - moles oxirane - moles hydroxy acetate) = (moles residual unsaturation). The mole fractions of oxirane, hydroxy acetate, and unsaturation are thus described.

The peracetic acid utilization is then described by

% conversion of peracid =

$$\frac{\text{mole fraction of functional group in product}}{(\text{moles peracetic acid})/(\text{moles initial unsaturation})} \times 100$$

Evaluation of Epoxidized Alkyllithium Polybutadienes as Plasticizers for Polyvinyl Chloride

(a) Formulation. The polyvinyl chloride formulation used in the evaluations was as follows:

Geon 101 EP (Goodrich PVC)	100 parts
Plasticizer	50 parts
Mark M (Argus), stabilizer	2 parts
Stearic acid, lubricant	0.5 part

The test methods are described below. The results of the evaluations are given in Tables 9, 10, and 11.

Table 9. Epoxidized Polybutadiene ($\overline{M}_n$ = 700, epoxy equiv. = 170) as a Primary Plasticizer for Polyvinyl Chloride

Plasticizer, 50 phr	Di-2-ethylhexyl phthalate (DOP)	Epoxidized soya oil Paraplex G-62[c]	Epoxidized polybutadiene
Original properties			
Tensile strength, psi	2600	2700	2690
Elongation, %	245	255	270
100% modulus, psi	1780	2040	1840
Shore A hardness	86	89	85
Low temperature properties			
Clash-Berg Temp., °C	-24	-12	-14
Permanence properties			
Activated carbon volatility, 70°C, 24 hr, % loss	1.4	0.7	1.0
Hexane extraction, 25°C, 1 hr, % loss	21	3.9	1.9
Soapy water extraction, 70°C, 20 hr, % loss	3.0	0.9	4.3
Compatibility			
Exudation in loop test after 1 day[a]	0	0	0
Thermal stability			
Color[b] after 15 min at 177°C	0	1	0
45	0	1	2
60	1	1	2
75	4	2	3
Ultraviolet light stability			
Hours to significant change	600	1000	700

[a] Code: 0 (none) to 5 (heavy).

[b] Code: 0 (colorless) to 5 (black).

[c] Rohm & Haas Co.

(b) Processing. A stirred mixture of plasticizer, resin, stabilizer, and lubricant was milled 8 min at 171°C on a two-roll mill. The resultant stock was sheeted off at about 0.080 in. thickness. The stock was molded at 177°C and 1500 psig into 6 X 6 X 0.070 in. and 6 X 6 X 0.010 in. pads. The molded vinyl formulations were allowed to stand at ambient conditions for 24 hr before testing.

(c) Test Methods. *Mechanical Properties.* Ultimate tensile strength, ultimate elongation, and modulus of elasticity at 100% elongation were determined at 24°C and 50% relative humidity on 0.070 in. dumbbells at a pulling rate of 20 in./min (ASTM D638-61T). Hardness was measured on 0.070 in. pads with a Shore A Durometer by taking a 15-sec reading (ASTM D1706-61).

Compatibility Loop Test. Strips (0.070 X 0.5 X 4 in.) were folded into loops. The loops were clamped securely in a two-plate steel clamp so that the peak of the loop extended 3/8 in. from the edge of the clamp. After one day, the strips were removed and the fold area was examined for exuded plasticizer. The samples were rated according to amount of exudation.

Ultraviolet Light Stability. Samples (0.010 in. film) were exposed to ultraviolet light in an Atlas Weather-O-Meter, Type DLTS-X, 65°C and 20% constant relative humidity. Changes with time were noted.

Suitable samples were evaluated in the following test procedures: Clash-Berg Temperature (ASTM D1043-61T), Carbon Black Volatility (ASTM D1203-61T), Hexane Extraction (ASTM D1239-55), Soapy Water Extraction (ASTM D1239-55), and Oven Heat Stability (ASTM D2115-62T).

RESULTS AND DISCUSSION

Epoxidation Studies

At any given number-average molecular weight alkyllithium polybutadienes prepared in the absence of donor molecules possess considerably lower bulk viscosities than sodium-initiated polybutadienes (cf. Fig. 1). Thus the sodium-initiated polybutadienes posses a much wider molecular weight distribution than the alkyllithium polybutadienes. The sodium and alkyllithium polybutadienes also differ markedly in microstructure. The sodium polybutadienes contain about 70% Type I unsaturation [13] while the alkyllithium polybutadienes can contain as much as 90% Type II

Table 10. Epoxidized Polybutadienes as Primary Plasticizers for Polyvinyl Chloride

Plasticizer, 50 phr	Di-2-ethylhexyl phthalate (DOP)	Epoxidized polybutadienes							
Molecular weight	390	790	700	680	750	720	2710	2400	2220
Epoxy equiv.	–	164	174	198	210	236	173	204	227
Original properties									
Tensile strength, psi	2750	2980	2700	2750	2580	Incompatible			
Elongation, %	265	285	280	265	255				
100% modulus, psi	1770	2010	1830	1870	1860				
Shore A hardness	86	86	85	85	91				
Low temperature properties									
Clash-Berg temp, °C	-24	-3	-14	-27	-30				
Permanence properties									
Activated carbon volatility, 70°C, 24 hr, % loss	1.4	0.7	0.8	1.4	1.8				

Hexane extraction, 25°C, 1 hr, % loss	20	0.5	1.5	6.4	11.1
Soapy water extraction, 70°C, 20 hr, % loss	3.4	6.6	4.1	2.0	2.8
Compatibility					
Exudation in loop test after 1 day[a]	0	0	0	5	Exudes before test
Thermal stability					
Color[b] after 15 min at 177°C	0	0	0	0	0
30	0	2	1	1	0
45	0	2	1	1	1
75	4	3	2	2	2
Ultraviolet stability					
Hours to significant change	500	600	600	600	–

[a] Code: 0 (none) to 5 (heavy).

[b] Code: 0 (colorless) to 5 (black).

Table 11. Epoxidized Polybutadines and Dioctyl Phthlate as Plasticizers for Polyvinyl Chloride

Plasticizer, 50 phr	Di-2-ethylhexyl phthalate (DOP)	Epoxidized polybutadienes							
MW	390	790	700	680	750	720	2710	2400	2220
Epoxy equiv.	–	164	174	198	210	236	173	204	227
% Replacement of DOP	0	50	50	50	50	50	50	50	50
Original properties									
Tensile strength, psi	2680	2790	2710	2860	2630	2660	2790	2490	2280
Elongation, %	275	280	255	285	280	280	245	230	145
100% modulus, psi	1700	1750	1830	1880	1740	1860	2110	1890	2060
Shore A hardness	84	83	84	86	86	88	89	89	92
Low temperature properties									
Clash-Berg temp, °C	-24	-12	-17	-25	-27	-31	-9	-18	-24
Permanence properties									
Activated carbon volatility, 70°C, 24 hr, % loss	1.1	0.9	1.0	1.0	1.1	1.5	0.8	0.9	0.9

Hexane extraction, 25°C, 1 hr, % loss	25	1.7	4.0	10.7	13.9	25	0.5	5.1	15.3
Soapy water extraction, 70°C, 20 hr, % loss	4.1	6.5	3.5	2.5	2.4	2.7	1.9	1.9	2.5
Compatibility									
Exudation in loop test after 1 day[a]	0	0	0	4	4	5	0	1	3
Thermal stability									
Color[b] after 15 min at 177°C	0	0	0	0	0	0	0	0	1
30	0	1	1	1	0	1	1	1	1
45	0	2	1	2	1	2	2	2	2
75	4	2	2	2	2	2	3	2	3
Ultraviolet stability									
Hours to significant change	500	800	–	–	800	300	800	800	800

[a] Code: 0 (none) to 5 (heavy).

[b] Code: 0 (colorless) to 5 (black).

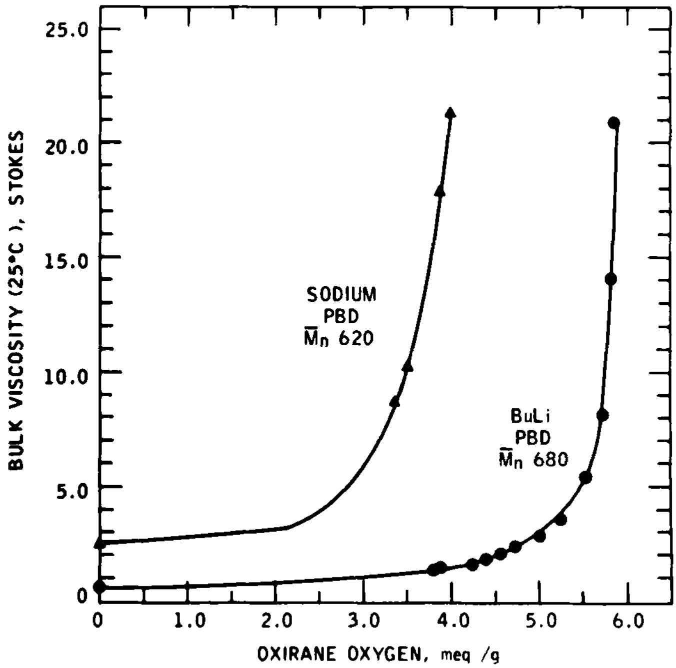

Fig. 2. Effect of epoxy content on bulk viscosity of epoxy polybutadiene.

unsaturation [14]. The higher rate of epoxidation of Type II unsaturation has been well established [4, 11, 12, 21].

In the initial stages of epoxidation of sodium-initiated polybutadiene the Type II unsaturation reacts almost exclusively at least until 15% of the available unsaturation is reacted (cf. Table 2). Most of this reactive Type II unsaturation is the trans form. Thus a polybutadiene containing predominantly Type II unsaturation would be expected to be readily epoxidized. Alkyllithium polybutadienes prepared in the absence of donor molecules contain 80-90% Type II unsaturation in the ratio of 2 trans/1 cis.

Four sodium-initiated polybutadienes were epoxidized with peracetic acid generated in situ to four levels of epoxy content. Epoxidations were effected to relatively low levels of epoxy. Our primary interest in these polymers was the effect of epoxy content on bulk viscosity. This effect is illustrated in Figs. 2 and 3. Viscosity increase is relatively low below epoxy contents of 3 mequiv./g, but between 3 and 4 mequiv./g a dramatic increase in bulk viscosity is experienced.

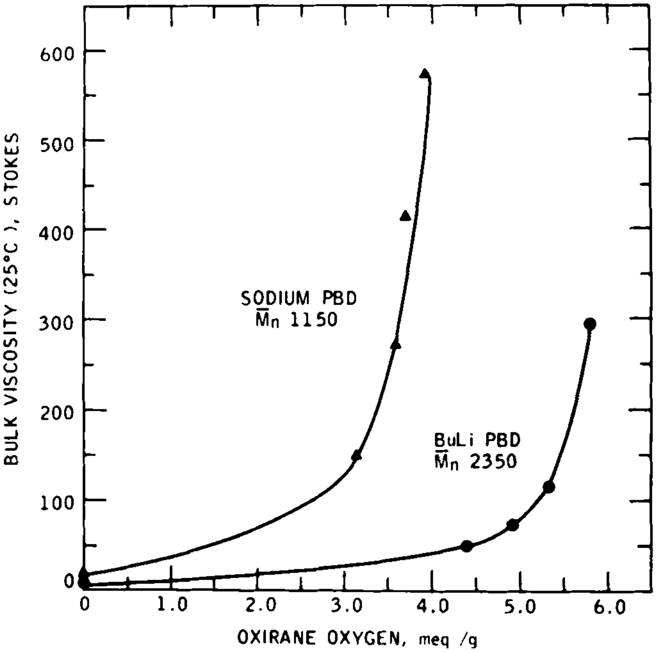

Fig. 3. Effect of epoxy content on bulk viscosity of epoxy polybutadiene.

Three alkyllithium polymers were studied, an $\bar{M}_n$ 680 polybutadiene, an $\bar{M}_n$ 2350 polybutadiene, and an $\bar{M}_n$ 750 butadiene–styrene block copolymer (20% styrene). All epoxidation studies with these polymers were made with aqueous peracetic acid. Aqueous peracetic acid differs from equilibrium peracetic in composition and also in that it contains no strong acid.

Toluene was chosen as a solvent for the epoxidation studies since the polymers are readily prepared therein. A reaction temperature of 60° and a peracetic acid addition time of 2 hr was used. Additional reaction beyond 30 min did not result in increased epoxy contents (cf. Table 3). The reaction of the peracetic acid is presumed to be rapid, but the peracetic acid which does not react probably is rather rapidly equilibrated at this temperature. Since increased reaction time did not provide increased epoxy content, an increase in epoxy content could be achieved only by using additional peracetic acid.

The effect of increasing peracetic acid concentration on resin epoxy content is illustrated in Figs. 4, 5, and 6. With the polybutadienes it appears that a maximum of 5.7-6.0 mequiv./g epoxy content is obtained

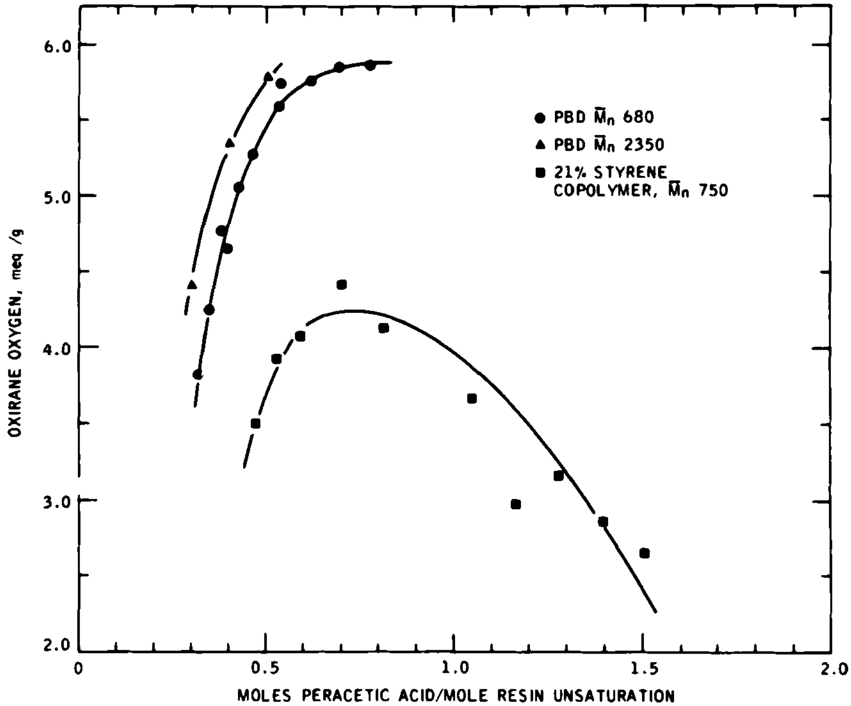

Fig. 4. Epoxidation of alkyllithium polymers. Effect of peracetic acid concentration on epoxy content.

corresponding to about 0.7 mole peracetic acid/mole unsaturation. With the butadiene–styrene copolymer a maximum of about 4.5 mequiv./g epoxy is reached at the same peracetic acid level, i.e., 0.7 mole peracetic acid/mole unsaturation. The $\bar{M}_n$ 680 polybutadiene and the 20% styrene copolymer had the same unsaturation composition, i.e., 17% Type I unsaturation, while the $\bar{M}_n$ 2350 polybutadiene contained less (15%) Type I unsaturation. This unsaturation difference is reflected in the higher epoxy contents of the $\bar{M}_n$ 2350 polybutadiene at any given peracetic acid level.

With the $\bar{M}_n$ 680 polybutadiene and butadiene–styrene copolymer a maximum in epoxy content is achieved at an unsaturation consumption of about 55%. The residual unsaturation becomes more difficult to epoxidize, and the conversion of epoxy with acetic acid to hydroxy acetate competes with epoxidation. However, with the aqueous peracetic acid system an unusual effect occurs. As peracetic acid is increased beyond 0.7 moles/mole

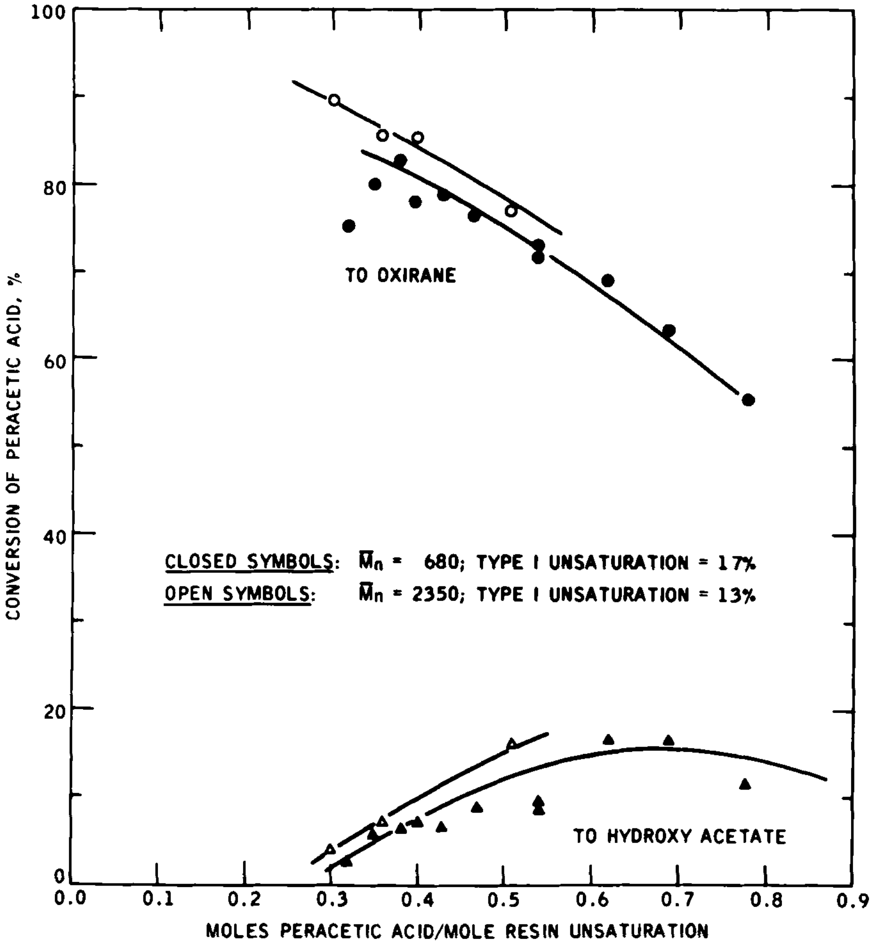

Fig. 5. Epoxidation of alkyllithium polybutadienes. Conversion of peracetic acid to polymer functionality.

unsaturation the comsumption of unsaturation decreases, i.e., both oxirane and hydroxy acetate contents decrease. Even though functional group content decreases, the bulk viscosity of the resin does not decrease; it continues to increase. The reduction in functionality is believed to be due to solubility effects. Aqueous peracetic acid is insoluble in toluene and for epoxidation to occur the toluene must extract out some peracetic acid to epoxidize in the toluene phase. However, as more peracid is added the amount

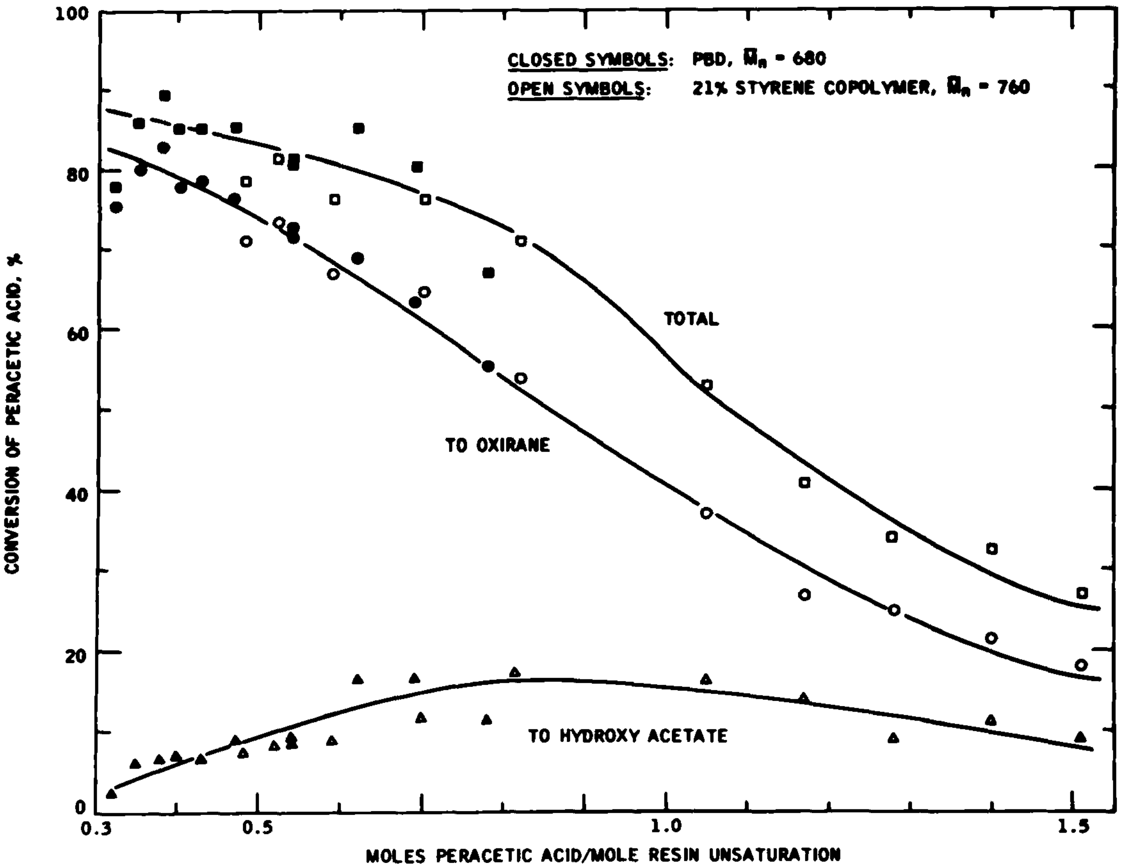

Fig. 6. Epoxidation of alkyllithium polymers. Conversion of peracetic acid to polymer functionality.

of aqueous phase increases and extraction of peracid from the aqueous phase as epoxidation proceeds becomes more difficult.

The increase in resin viscosity with increasing peracetic acid must mean that epoxy polymerization is occurring. Under these conditions, even though epoxy and hydroxy acetate contents decrease, a molecular weight buildup results, thereby increasing resin viscosity. Thus further increases in peracetic acid concentration is detrimental, i.e., the epoxy content decreases while the bulk viscosity of the resin increases.

The peracetic acid used in these studies had a typical composition of 27% peracid, 20% acetic acid, and 5% H_2O_2. Aqueous peracetic acid containing 40% peracid, 15% acetic acid, and virtually no H_2O_2 is easy to generate [19]. With this higher strength peracetic acid composition it would be expected that the maximum epoxy contents obtainable would increase for two reasons: 1) less epoxy ring opening with acetic acid, and 2) higher degree of unsaturation consumption due to the corresponding reduction in aqueous phase.

In polybutadiene epoxidations the initial introduction of epoxy results in small increases in viscosity, but a point is reached where further increases in epoxy content results in almost catastrophic viscosity increases. It is clear that this severe viscosity increase is a direct result of molecular weight buildup of the epoxy resin due to epoxy polymerization. Catastrophic viscosity increases can be avoided to some extent by variation of epoxidation conditions and by using more reactive unsaturation in the epoxidation. Obviously the introduction of less epoxy will also avoid the large viscosity increases. Although this is obvious, it takes on new meaning with alkyllithium polybutadienes.

Alkyllithium polymers have low viscosities to start, and they are high in Type II, expecially trans, unsaturation. Thus they are more readily epoxidized. Also since the viscosities are low it is possible to operate at much higher number-average molecular weights. This is illustrated in Figs. 2 and 3 where bulk viscosity is plotted against oxirane content. In both cases the alkyllithium polybutadiene has the higher molecular weight but lower viscosity at any level of epoxy. This is especially dramatic in Fig. 3 where an alkyllithium polybutadiene of M_n 2500 is compared with a sodium polybutadiene of M_n 1200. The epoxy level at which severe viscosity increases are encountered is much lower (3-4 mequiv./g) for sodium-initiated polybutadienes than for alkyllithium polybutadienes (5-6 mequiv./g). The differences in viscosity increase observed do not just apply to the molecular weight differences. Even when the bulk viscosity of the starting sodium polybutadiene is lower than the starting alkyllithium polybutadiene (which means a significant number-average molecular weight difference) the bulk viscosity of the epoxidized sodium polybutadiene becomes significantly higher than the alkyllithium polybutadienes (cf. Tables 2 and 8). An $\bar{M}_n$ 2350 polybutadiene with starting viscosity of 8.4 St achieves a viscosity of 48 St at an epoxy content of 4.4 mequiv./g. A sodium polybutadiene of M_n 780 with a starting viscosity of 5.0 St achieves a higher viscosity (65.3 St) at lower epoxy content (4.1 mequiv./g), and these viscosity differences will become much larger with increasing epoxy contents. Thus there can be little doubt that polybutadiene microstructure influences this viscosity increase; the higher the Type I unsaturation, the higher the viscosity increase. This effect is believed to be related to 1) lower reactivity of Type I unsaturation to epoxidation, and 2) greater reactivity of terminal epoxides to polymerization compared to internal epoxides.

Thus changes in polybutadiene microstructure alone permit reductions in epoxy resin viscosities. As was noted previously, the catastrophic viscosity increases experienced during epoxidation are not accompanied by correspondingly large increases in epoxy content, and the increased resin viscosity itself offers no advantage for resin reactivity or utility. This viscosity increase is best avoided. Low viscosity epoxy polybutadienes are readily prepared by using low viscosity (but high $\bar{M}_n$) alkyllithium polybutadienes which are more easily epoxidized to high epoxy levels with lower viscosity buildup.

In thermoset applications the higher $\bar{M}_n$ of alkyllithium polybutadienes for a given bulk viscosity can be significant in another way. For two different molecular weight resins identical in epoxy content it is expected that the higher $\bar{M}_n$ resin will give the highest cross-link density and a better cured network. It then follows that a higher $\bar{M}_n$ resin will require less epoxy for the same cross-link density as the lower $\bar{M}_n$ resin. The lower epoxy requirement in turn means a reduction in resin viscosity as discussed above.

Thus at equivalent resin viscosities it will be possible to raise $\bar{M}_n$ even further. The viscosity increases associated with the higher epoxy levels are appreciable. In Figs. 2 and 3 it is seen that increasing epoxy content from 5.0 to 5.5 mequiv./g doubles resin viscosity. Further epoxy content increases result in substantially greater viscosity increases.

If an epoxy polybutadiene of $\bar{M}_n$ 1200 requires an epoxy content of 5.7 mequiv./g, then an epoxy polybutadiene of $\bar{M}_n$ 2400 should require an epoxy content of about 5.0 mequiv./g to achieve the same level of cross-link density. Here it is assumed that one epoxy on each of two chains of the $\bar{M}_n$ 1200 polymer are required to react to achieve a molecular weight equivalent to the $\bar{M}_n$ 2400 resin. As the molecular weight of the resin increases the epoxy requirement should decrease even further.

It is possible to prepare $\overline{DP}$ 100 ($\bar{M}_n$ 5400) polybutadienes possessing viscosities of between 50 and 75 St. From what we have seen with alkyllithium polybutadienes it is possible to prepare epoxy polymers of this molecular weight with an epoxy content of 5.0 mequiv./g and still have a resin viscosity near 1000 St. Thus it would appear that epoxy resins with good cure properties can be readily prepared from a polybutadiene with $\bar{M}_n$ 5000 at an epoxy content of 5.0 mequiv./g. If the above is indeed true, then the lower epoxy requirements for higher molecular weight resins have an important influence on peracetic acid utilization and the epoxidation process. To achieve an epoxy content of 5.0 mequiv./g requires about 0.36-0.37 moles peracetic acid/mole unsaturation in an $\bar{M}_n$ 2350 polybutadiene (cf. Table 8). At this peracetic acid level 85% of the peracid is converted to oxirane and 7-10% to hydroxy acetate, for a total utilization of 95% (cf. Table 8 and Fig. 5). To achieve an epoxy content of 5.7 mequiv./g requires double the amount of peracetic acid, i.e., 0.7 moles peracetic acid/mole unsaturation, and under these conditions only 77% of the peracetic acid is converted to epoxy. The differences in peracetic acid requirements are substantial.

In our epoxidation studies we chose toluene as the solvent because alkyllithium polybutadienes with the lowest viscosities and highest Type II structures are obtained therein. Further, by utilizing the Attapulgus clay technique [14], it is possible to prepare the polybutadienes in toluene solvent, add the clay, filter, and have a solution ready for epoxidation. Since any molecular weight polybutadiene can be prepared in this way, a systematic study of epoxidation and molecular weight effects can be made conveniently.

The alkyllithium polymerization permits the preparation of a very interesting polybutadiene [14-16]. Although it has already been shown that the reactivity of unsaturation in polybutadiene is in the order Type II trans > Type II cis > Type I [4, 11, 12, 21], epoxidation studies on polybutadienes have not been very quantitative due to composition imbalances. With alkyllithium in an aliphatic solvent it is possible to prepare a $\overline{DP}$ 10 polybutadiene having approximately equal modes of unsaturation, i.e., Type I 34%, Type II cis 27%, and Type II trans 29%. Such a polymer is ideally suited for studying competitive epoxidations.

Epoxidized Polybutadienes as Plasticizers for Polyvinyl Chloride

Epoxidized derivatives of unsaturated fatty acid esters have been used for about 20 years as plasticizers and stabilizers for polyvinyl chloride [22, 23]. The most commonly used types are triglycerides, such as epoxidized soybean oil, and mono-esters, such as epoxidized octyl tallate [24, 25]. The market for these materials has grown substantially [26]. However, a continuing problem with these esters has been the introduction of a sufficient number of epoxy groups into the molecule. This is important as it is necessary to introduce sufficient functionality into an otherwise incompatible ester so that it becomes compatible with the polyvinyl chloride resin [24, 25]. The importance of this is emphasized by the more recent development of dialkyl epoxyhexahydrophthalates as completely compatible plasticizers [27].

Epoxidized alkyllithium polybutadienes are new raw materials for this application and offer the advantage of wide variations in molecular weight and epoxy content to obtain various plasticizer properties. In addition a high level of epoxy oxygen can be introduced (5-10%) compared to the conventional epoxy plasticizers (4-6%).

The effect of varying both the molecular weight and the epoxy content of the epoxy alkyllithium polybutadienes on compatibility is shown in Tables 12 and 13. When the epoxidized polybutadienes are used alone in polyvinyl chloride, compatibility is a direct function of both epoxy content and molecular weight. It is evident that the lower molecular weight polymers are compatible to an epoxy equivalent of 180-190 and are primary plasticizers. One such epoxidized polybutadiene is compared as a primary plasticizer with di-2-ethylhexyl phthalate and an epoxidized soya oil in Table 9.

Table 12. Compatibility of Epoxidized Polybutadienes as Sole Plasticizer for Polyvinyl Chloride

Molecular weight of polybutadiene	680	680	680	680	680	2350	2350
Epoxy equiv., MW/epoxy group	164	174	198	210	236	173	204
Compatibility, exudation in loop test	None	None	Heavy	Exudes before test	Incompatible		

When used at a level of 50% replacement of di-2-ethylhexyl phthalate, materials of higher molecular weight become compatible, and compatibility becomes a function of epoxy content alone (at least in the molecular weight range tested) as shown in Table 13. Since the epoxy group is virtually the only functional group present and the polybutadienes are incompatible by themselves, it is understandable that the epoxy content plays such a key role. This suggests that even higher molecular weight samples of these polybutadienes will be useful plasticizers. This is in significant contrast to reports in the literature where the optimum concentration was 5% replacement of dioctyl phthalate for epoxidized polybutadienes and styrene–butadiene copolymers derived from conventional sodium-catalyzed polymerization [28].

Table 13. Compatibility in Polyvinyl Chloride of Epoxidized Polybutadiene 1:1 with Dioctyl Phthalate

Molecular weight of polybutadiene	680	680	680	680	680	2350	2350	2350
Epoxy equiv., mw/epoxy group	164	174	198	210	236	173	204	227
Compatibility, exudation in loop test	None	None	Moderate	Moderately heavy	Heavy	None	Very light	Light

Another significant property of these epoxy polybutadienes is good plasticizing efficiency. This property appears to be essentially a function of molecular weight, as it holds rather constant for materials made from the same polybutadiene regardless of epoxy content. For example, the series of epoxy polybutadienes made from a polybutadiene of $\bar{M}_n$ 680 gave 100% moduli of 1740 to 1880 lb/in.^{2} when used 1:1 with dioctyl phthalate, while the series made from the $\bar{M}_n$ 2350 polybutadiene gave 100% moduli of 1890-2110 lb/in.^{2} (see Table 11). For comparison, dioctyl phthalate when used by itself gave 100% modulus of 1700 lb/in.^{2}

The permanence properties of the epoxidized polybutadienes are good and follow a more predictable pattern. The volatility appears to be simple inverse function of molecular weight. The extraction resistance is partly a function of molecular weight, but is much more dependent on the polarity of the molecule as indicated by the epoxy content. Thus, extraction by soapy water increases with epoxy content, while extraction by hydrocarbons decreases. Over-all, their permanence and compatibility are similar to those of the epoxy soya oils and better than those of the epoxy tallates.

The thermal stability of the epoxidized polybutadienes in polyvinyl chloride is good and, rather surprisingly, appears to be independent of epoxy content. All of the plasticized compounds reached a yellow color within 45 min in the 177°C oven stability test, but then resisted further change, while polyvinyl chloride with dioctyl phthalate alone turns brown after 75 min. This is similar behavior to that reported for the dialkyl epoxyhexahydrophthalates [27]. Also, variations in behavior between samples that should be expected to behave similarly are often due to impurities remaining after synthesis [24].

The ultraviolet light stability of these materials in polyvinyl chloride also appears to be good. Most of them begin to turn yellow after about 800 hr of exposure in a Fadeometer. However, they do not show the pitting that dioctyl phthalate plasticized vinyl samples show. Thus, these epoxidized polybutadienes show good plasticizer properties and represent one of the few examples where a hydrocarbon has been converted in one step to a primary plasticizer.

ACKNOWLEDGMENTS

The authors are indebted to Messrs. Robert E. O'Brien, Frederick J. Radloff, Robert J. French, and Salvatore J. Pace for their expert experimental assistance. Information from the FMC Corp. laboratories in Princeton, N. J., regarding a bench scale aqueous peracetic acid generator is gratefully acknowledged.

REFERENCES

[1] F. P. Greenspan and R. E. Light, Jr. (to FMC Corporation), U.S. Patent 2,829,130 (April 1, 1958).
[2] F. P. Greenspan and A. E. Pepe (to FMC Corporation), U.S. Patent 2,829,131 (April 1, 1958).
[3] F. P. Greenspan and R. E. Light, Jr. (to FMC Corporation), U.S. Patent 2,833,747 (May 6, 1958).
[4] C. E. Wheelock, *Ind. Eng. Chem.*, **50**, 299 (1958).
[5] F. P. Greenspan and R. E. Light, Jr. (to FMC Corporation), U.S. Patent 2,829,135 (April 1, 1958).

[6] F. P. Greenspan, C. Johnston, and M. Reich, *Mod. Plast.*, **37**, 142 (1959).
[7] C. E. Wheelock and P. J. Canterino (to Phillips Petroleum Co.), U.S. Patent 3,022,322 (February 20, 1962).
[8] C. E. Wheelock (to Phillips Petroleum Co.), U.S. Patent 3,028,370 (April 3, 1962).
[9] A. D. Theodor, *Polimery*, 8,97 (1963); *Chem. Abstr.*, **59**, 14164b (1963).
[10] Th. Andrei, *Rev. Chim. (Bucharest)*, **14**, 328 (1963); *Chem. Abstr.*, **59**, 12982a (1963).
[11] V. N. Gorbunov, S. S. Rydvanova, and G. I. Zalkind, *Plast. Massy*, **1964**, 7; *Chem. Abstr.*, **61**, 14847 (1964).
[12] V. N. Gorbunov, S. S. Rydvanova, and G. I. Zalkind, *Plast. Massy*, **1966**; 13.
[13] W. W. Crouch and J. A. Shotton, *Ind. Eng. Chem.*, **47**, 2091 (1955).
[14] H. S. Makowski and M. Lynn, *J. Macromol. Chem.*, **1**, 443 (1966).
[15] H. S. Makowski, M. Lynn, and A. N. Bogard, *J. Macromol. Sci.–Chem.*, **A2**, 665 (1968).
[16] H. S. Makowski and M. Lynn, *J. Macromol. Sci.–Chem.*, **A2**, 683 (1968).
[17] DuPont Bulletin P 61-454, *Hydrogen Peroxide-Resin Technique for Epoxidation of Unsaturated Fats, Oils and Derivatives*, April, 1954.
[18] A. J. Durbetaki, *Anal. Chem.*, **28**, 2000 (1956).
[19] FMC Corporation, Inorganic Chemicals Division, *The Operation of a Bench Scale Peracetic Acid Generator and Typical Applications of Generator Peracid*, 1963.
[20] J. A. John and F. J. Weymouth, *Chem. Ind.* (London), **1962**, 62.
[21] D. Swern, "Epoxidation and Hydroxylation of Ethylenic Compounds with Organic Peracids," in *Organic Reactions*, Vol. 7, Wiley, New York, Chap. 7.
[22] J. G. Wallace, in *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd ed., Vol. 8, Wiley- (Interscience), New York, 1965.
[23] D. C. Swern, *Paint Varn. Prod.*, **46**, 35 (1956).
[24] L. P. Witnauer, H. B. Knight, W. E. Palm, R. E. Koos, R. E. Ault, and D. C. Swern, *Ind. Eng. Chem.*, **47**, 2304 (1955).
[25] F. P. Greenspan and R. J. Gall, *Ind. Eng. Chem.*, **45**, 2722 (1953).
[26] *Mod. Plast.*, **46**, 207 (1967).
[27] F. P. Greenspan and R. J. Gall, *Ind. Eng. Chem.*, **50**, 865 (1958).
[28] W. P. Fitzgerald and P. V. Smith (to Esso Research & Engineering Co.), U.S. Patent 2,842,513 (July 8, 1958).

Accepted by editor January 6, 1970
Received for publication March 16, 1970