

Investigations on the Curing of Epoxides with Phthalic Anhydride

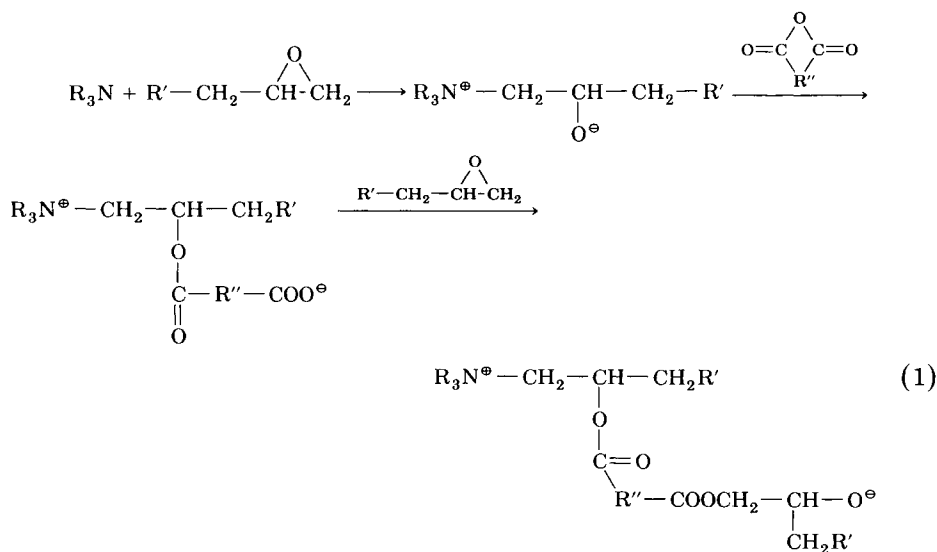
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Synopsis

The anhydride curing of epoxides was studied by performing copolymerizations of epichlorohydrin, phenyl glycidyl ether (PGE), or bisphenol-A-diglycidyl ether (BADGE) with phthalic anhydride (PSA). As initiators, tertiary amines or ammonium salts were used. In the case of epichlorohydrin, linear polyesters were obtained at 100°C. At higher temperatures (140–160°C), a side reaction of the CH₂Cl group took place which caused branching and partial crosslinking of the polymer. The reaction of phenyl glycidyl ether with phthalic anhydride gave linear, strongly alternating copolymers at temperatures of 120–160°C. Molecular weights (\bar{M}_n) were in the range of 4000–87,000, depending on the purity of the starting materials and the initiator used. The reaction of the diepoxide BADGE with phthalic anhydride yielded highly crosslinked products. Their crosslink densities (which correlate with the glass transition temperature T_g), however, did not show the same dependence on initiator and purity of the starting materials as the molecular weights of the linear polyesters obtained by the “model reaction” of PGE with PSA. Possible reasons for this effect are discussed.

INTRODUCTION

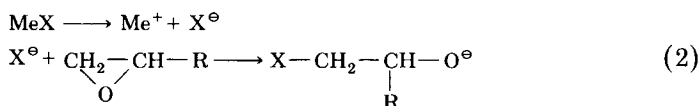
The anhydride curing of epoxy resins, catalyzed by tertiary amines, is an alternating copolymerization yielding linear polyesters if monoepoxides are used or crosslinked polyesters by employing diepoxides. The idealized polymerization mechanism can be described by a reaction sequence that has been proposed by Matejka et al. from investigations of model compounds¹:



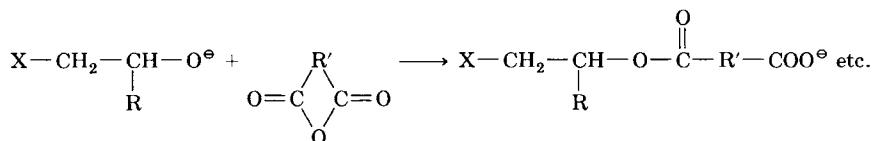
Detailed studies on the curing of epoxides with hexahydrophthalic anhydride (HHPA), however, showed that the polymerization was complicated by some chain anhydride formation and an isomerization reaction of the anhydride which was responsible for the low molecular weights and some special features in the NMR spectra of the polymers.^{2,3} In order to study the "pure" anhydride curing of epoxides, it is therefore necessary to use another anhydride that does not undergo any side reaction. For this aim, phthalic anhydride (PSA) seemed to be the best candidate. Fischer already reported copolymerization experiments of this anhydride with epichlorohydrin, allyl glycidyl ether, or ethylene oxide which yielded polyesters with molecular weights (\bar{M}_n) of up to 18,400.⁴ This is considerably higher than the results that were obtained from our experiments with HHPA ($\bar{M}_n \sim 3000$).³

Schwenk et al. performed copolymerizations of monoepoxides or cyclic carbonates (which yield epoxides at higher temperatures) by using organic and especially inorganic salts as catalysts.⁵ The highest molecular weight of $\bar{M}_n = 50,000$ was obtained with 0.5 mol % of LiCl at 200°C. Experiments with ¹⁴C-marked Na-benzoate⁶ showed that the initiator was incorporated into the polymer chain. This is consistent with the following anionic mechanism⁵:

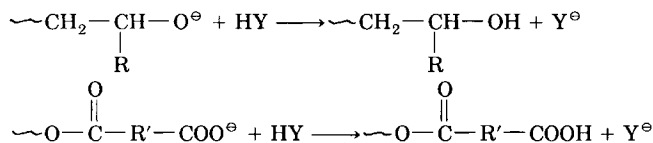
Initiation:



Propagation:



Termination:



The termination is a transfer reaction with some compound containing active hydrogen, like water, diol, or an acid.

Recently, Aida et al.^{7,8} described a catalyst system that effected "living polymerization" of monoepoxides with phthalic anhydride. This catalyst was an aluminium porphyrin coupled with a quarternary organic salt, particularly a phosphonium salt. Copolymers with a very narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n \approx 1.1$) were obtained. As rather high catalyst concentrations of 2 mol % were used, molecular weights were only in the range 2700–7000.

This rather complicated catalyst, as well as inorganic salts, however, is not used for the curing of epoxy resins with anhydrides for technical purposes.

LiCl, for example, is too insoluble and not reactive enough at temperatures below 200°C to find any practical application. Therefore, the emphasis of the present investigations was put on the copolymerization of epoxides and anhydrides initiated by tertiary amines and ammonium salts, compounds that are widely used for the curing of diepoxides with anhydrides. Conditions were found that allowed the preparation of very high molecular weight PGE/PSA copolymers with some of these initiators. Correlations were sought between the results from the copolymerization of phenyl glycidyl ether and PSA and the characteristic features that are observed by crosslinking bisphenol A diglycidyl ether (BADGE) with PSA by using the same catalysts. Furthermore, some surprising results are reported that were obtained when it was tried to reproduce some of Fischer's experiments on the copolymerization of epichlorohydrin and PSA.

EXPERIMENTAL

Epichlorohydrin was distilled before use (purity > 99.9% by GC). Phenyl glycidyl ether (PGE) was distilled over calcium hydride at reduced pressure (purity > 99.9% by GC). Bisphenol-A-diglycidyl ether (BADGE) was crystalline with a melting point of 41–42°C (purity > 99.9% by GC). Phthalic anhydride (PSA), which was recrystallized once from toluene, contained about 0.2 mol % acid. For the preparation of practically acid-free anhydride, a solution of 30 g PSA in dioxane, containing about 6 mL of thionyl chloride, was refluxed for 2 h.⁵ Then, the thionyl chloride was evaporated and the residue was recrystallized twice from toluene. The acid content of the product was 0.0017 mol/kg = 0.025 mol % (determination by titration with 0.1*N* tripropylamine in acetone).

Benzyltrimethylamine (BDMA) and 1-methylimidazole (1-MI) were distilled at reduced pressure (purity > 99.5% by GC). Tetraethylammoniumbromide (TEAB), tetrabutylammoniumbromide (TBAB), and tetrabutylammoniumiodide (TBAI) (Fluka, puriss) were used after drying at 100°C without further purification.

The copolymerizations of epichlorohydrin or phenyl glycidyl ether with PSA and different catalysts were carried out in bulk in a flask equipped with stirrer and thermometer, in a nitrogen atmosphere at 100–200°C. For the preparation of PGE/PSA copolymers of high molecular weight, distilled PGE was dried again over calcium hydride overnight. It was then introduced by distillation into the dried reaction flask, cooled with a liquid nitrogen bath. After addition of PSA and the initiator the reaction mixture was stirred under nitrogen at 140°C for 8 h. The products were reprecipitated two or three times from dichloroethane/ether and dried *in vacuo* at 60°C.

The curing reactions of BADGE and PSA with different catalysts were performed either in closed reactions flasks, which were immersed into an oil bath, in a nitrogen atmosphere or in open reaction vessels in an oven, preheated to the desired temperature.

The ¹H- and ¹³C-NMR spectra were recorded on a Bruker SY 100 WP or AM-300 instrument. Molecular weights were determined by GPC on a Waters Liquid Chromatograph equipped with an RI detector. Three columns (7 × 300 mm) filled with Ultra Styragel of pore sizes 1000, 500, and 100 Å were

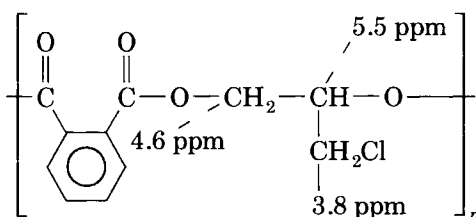
connected in series and calibrated by a polystyrene standard. DSC measurements were carried out on a Mettler-TA 3000 instrument with a heating rate of 10 K/min under nitrogen (~ 50 mL/min).

RESULTS AND DISCUSSION

Copolymerization of Epichlorohydrin and PSA

The copolymerization of epichlorohydrin and PSA was performed in bulk with 0.2 mol % of BDMA as catalyst. Experiments that were carried out at 100°C for 5 h yielded products of $\bar{M}_n = 8800$ –12,500 and $\bar{M}_w = 17,000$ –23,500 (Table I). This corresponds roughly to the results obtained by Fischer using similar conditions ($\bar{M}_n = 2700$ –11,500).⁴ When the reaction was performed during 5 h at 100°C and 1 day at 160°C, i.e., under reaction conditions that were applied by Fischer to produce polyesters with the highest molecular weight of 18,400,⁴ polymers were obtained with \bar{M}_n of 20,000–25,000, but \bar{M}_w of 200,000–500,000 (Table I). The extremely broad molecular weight distribution and the partial insolubility of one of the products indicated that at higher temperature some side reaction had occurred which caused such an extreme change in the polymer properties.

The ¹H-NMR spectrum of the polyester from the reaction at 100°C [Fig. 1(a)] shows three signals at 3.8, 4.6, and 5.5 ppm, besides the peaks of the aromatic nucleus at 7.5–7.7 ppm. These signals can be assigned to the CH₂Cl —, CH₂OOC —, and CHOOC — groups of the expected polyester structure with correct ratios of the peak areas.



A slightly different spectrum is obtained from the high-temperature product

TABLE I
Copolymerization of Epichlorohydrin with PSA (1 : 1 mol/mol) Reaction Conditions and Molecular Weights

Catalyst	Reaction conditions	\bar{M}_n	\bar{M}_w	Remarks
0.2 mol % BDMA	5 h, 100°C	8800	17,000	Epichlorohydrin used without distillation
0.2 mol % BDMA	5 h, 100°C	12,500	23,500	Distilled epichlorohydrin
0.2 mol % BDMA	5 h, 100°C + 24 h, 160°C	20,000	200,000	Epichlorohydrin not distilled
0.2 mol % BDMA	5 h, 100°C + 24 h, 160°C	25,300	500,000	Distilled epichlorohydrin, product partly soluble

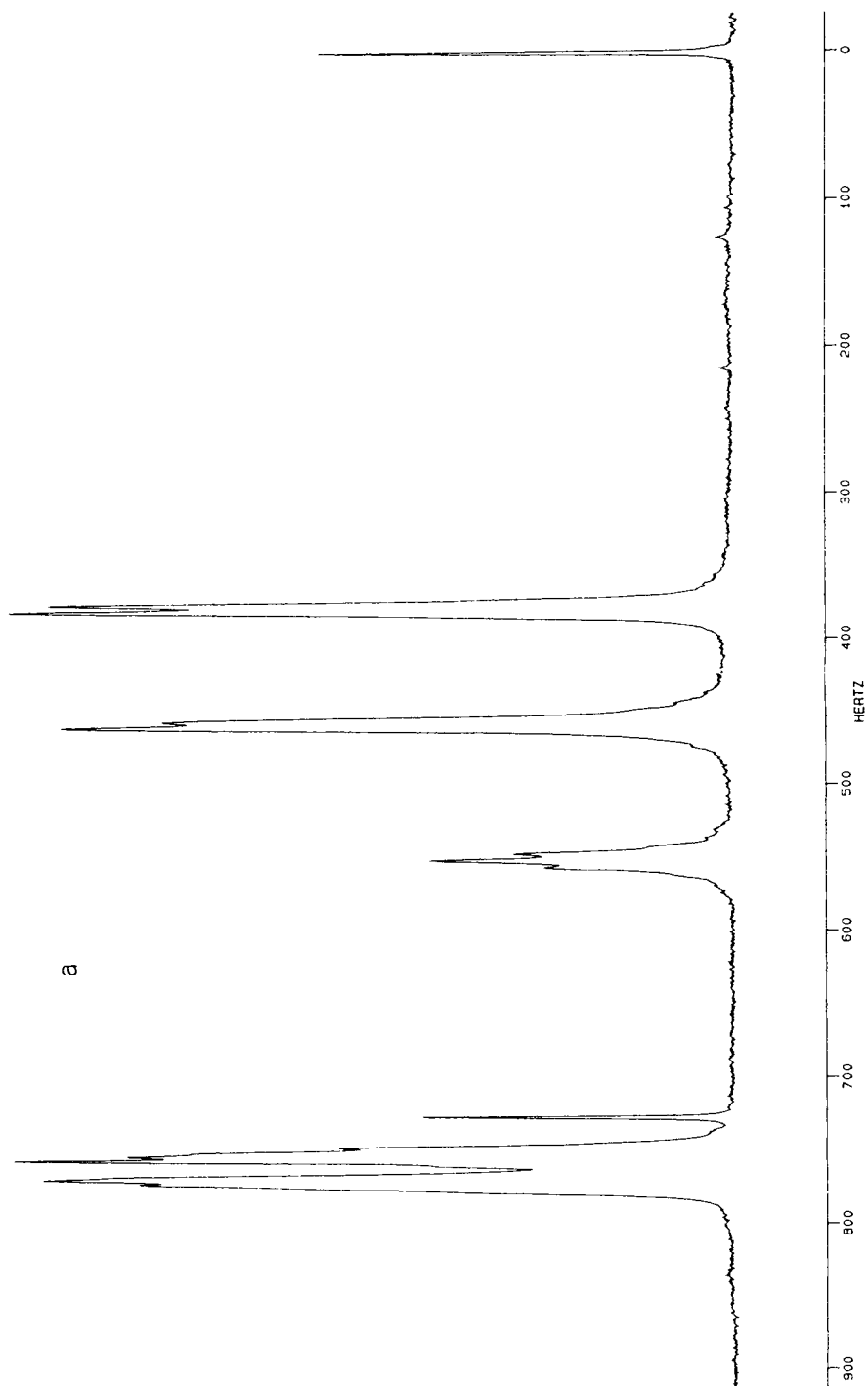


Fig. 1. ¹H-NMR spectra of epichlorohydrin/PSA copolymers in CDCl₃: (a) polymerization at 100°C, 5 h; (b) polymerization at 100°C, 5 h and 160°C, 24 h.

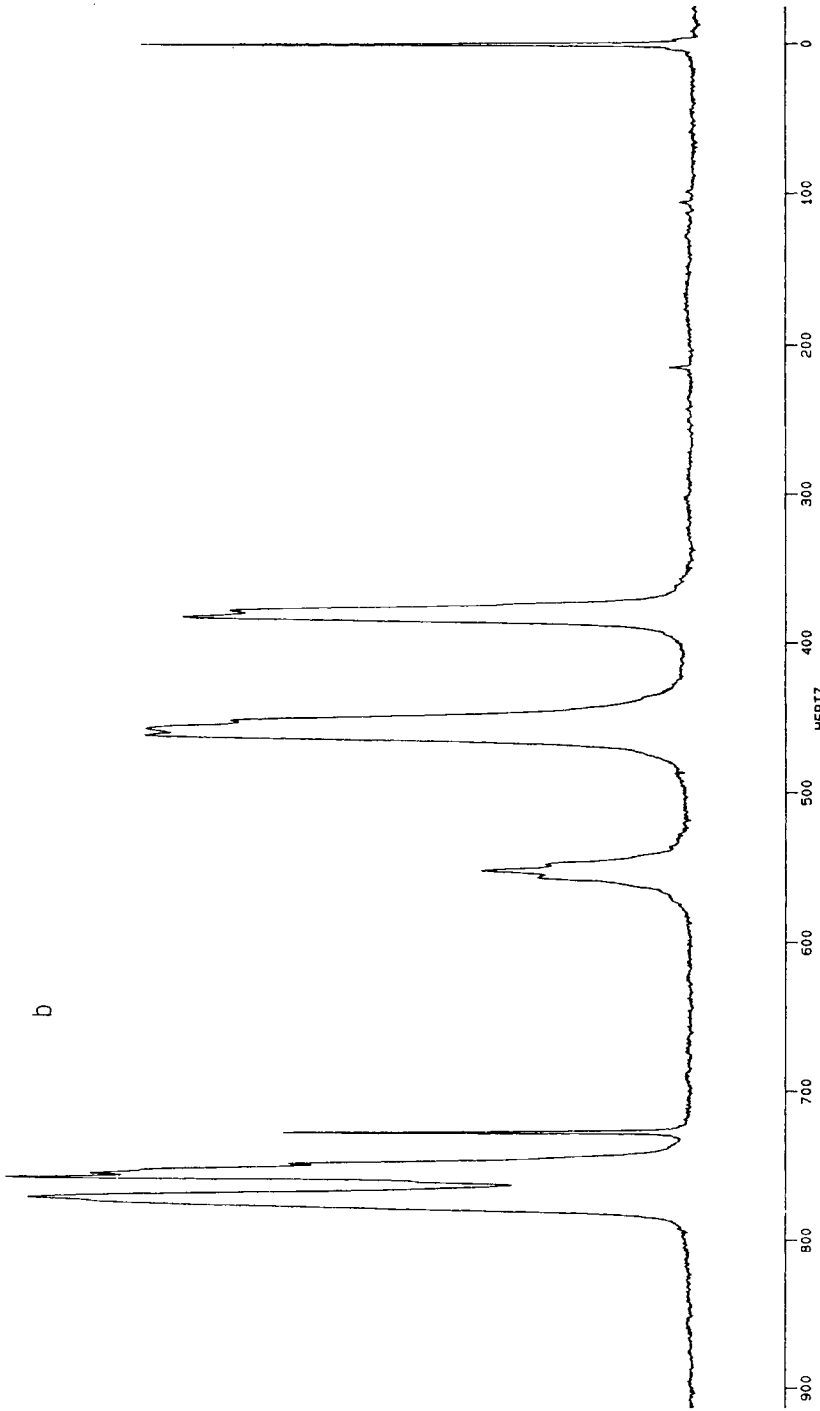
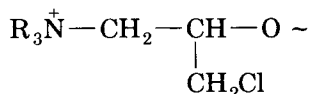


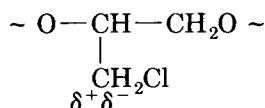
Fig. 1. (Continued from the previous page.)

[Fig. 1(b)]. At 4.5 ppm, a shoulder points to the formation of a new peak which overlaps partly with the signal of the CH₂O — group, and the areas of the peaks at 3.8 and 5.5 ppm are reduced compared to the aromatic peaks which may serve as internal standard. The ¹³C-NMR spectrum of the polymer shows the appearance of two new peaks at 54.7 (D) and 65.6 (T) ppm [Figs. 2(a) and (b)].

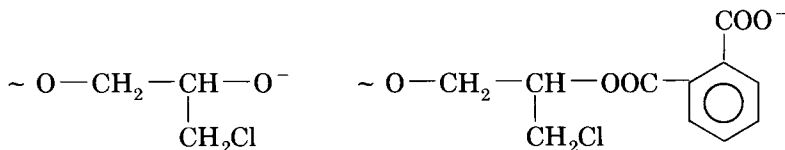
The microanalysis is almost identical for the two polymers (C 54.80%, 54.87%, H 3.89%, 3.91%, Cl 14.51%, 14.20%, calcd: C 54.90%, H 3.77%, Cl 14.73%). How can these results be explained? Possibilities of side reactions at elevated temperature are given by several active groups in the reaction mixture which include the ammonium ion of the initiation reaction,



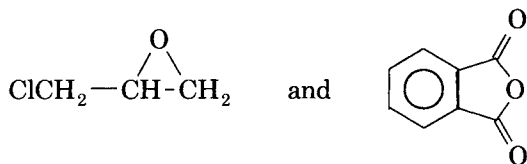
the CH₂Cl — side groups,



and the carboxylate and alkoxide anions,

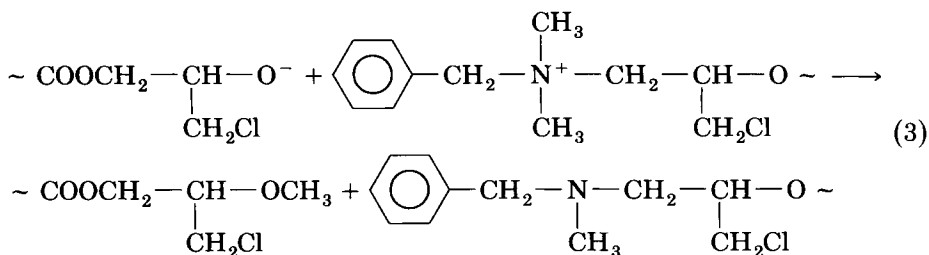


The free monomers



must also be included in this list. As the temperature is raised only after the reaction has already been performed during 5 h of 100°C, i.e., after almost total completion, only a few monomers are still available for side reactions at this time.

The ammonium ion could cause the following termination reaction:



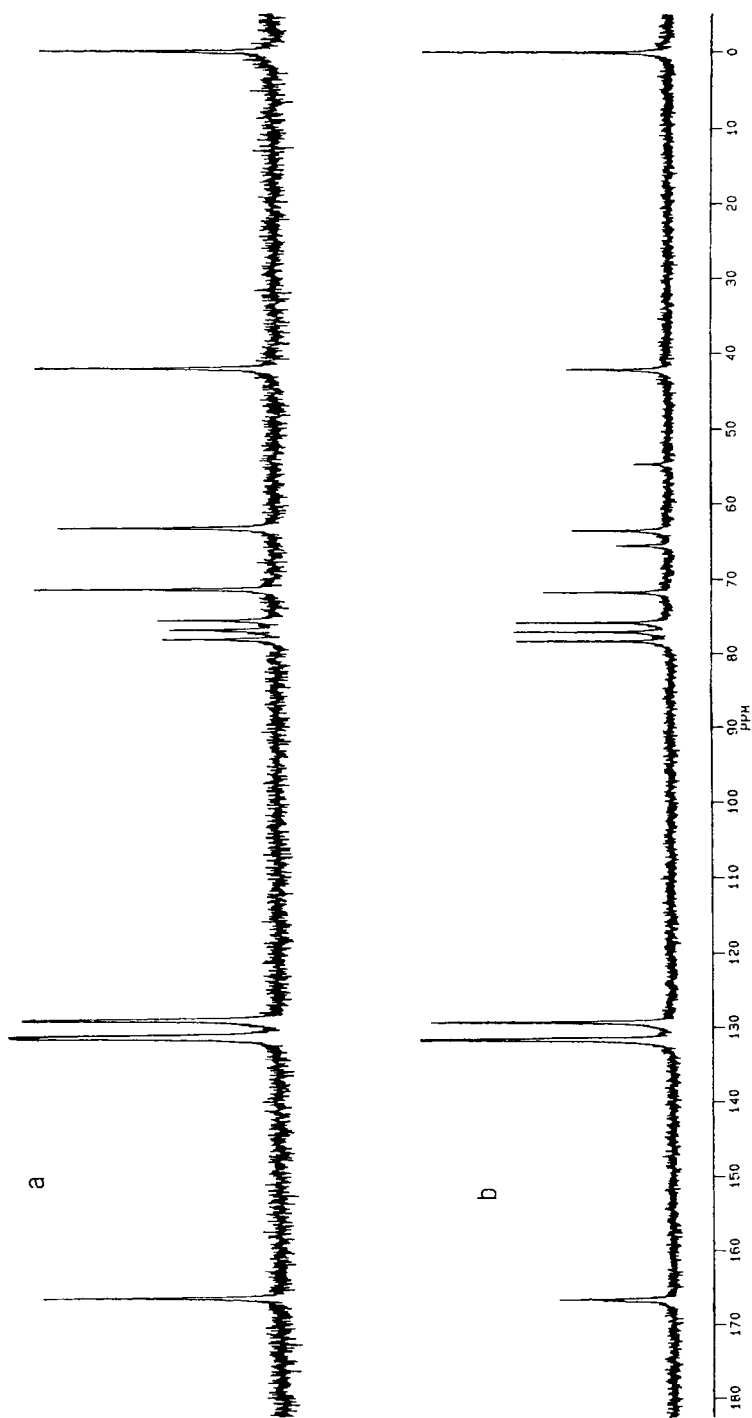
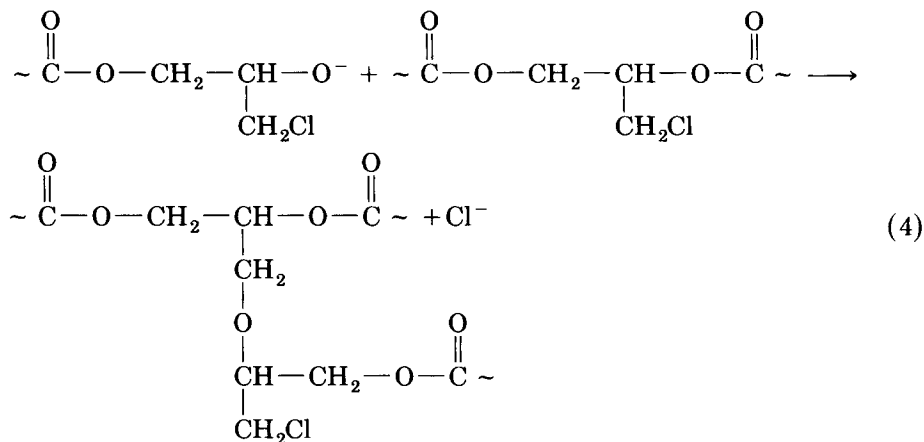
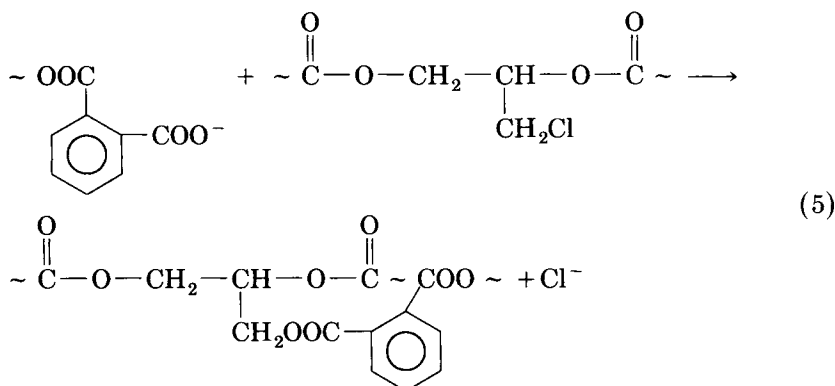


Fig. 2. ^{13}C -NMR spectra of epichlorohydrin/PSA copolymers, in CDCl_3 : (a) polymerization at 100°C , 5 h; (b) polymerization at 100°C , 5 h and 160°C , 24 h.

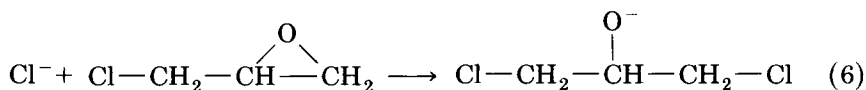
The reaction of an alkoxide or carboxylate anion with the CH_2Cl — group of the polyester would lead to branching of the polymer chain:



or



The Cl^- could find an unreacted epichlorohydrin to give:



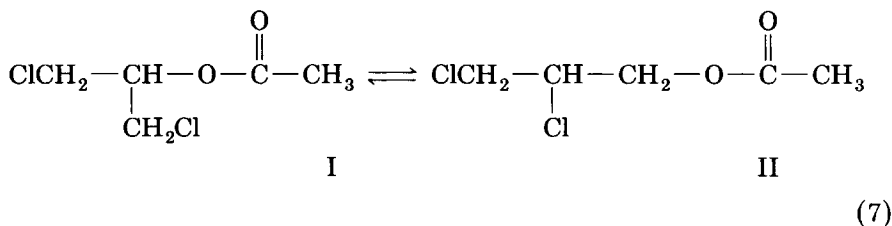
which could react further to give low molecular weight material or terminate via proton capture.

This large quantity of possible side reactions should give quite a complicated NMR spectrum. As described before the ^1H -NMR spectrum only shows one new peak at 4.5 ppm, the ^{13}C -NMR spectrum has two new intense peaks at 54.7 and 65.6 ppm. There are a few other very small signals at 73, 71, 64, 55.5, 50, and 43 ppm which must belong to products in concentrations of < 10%.

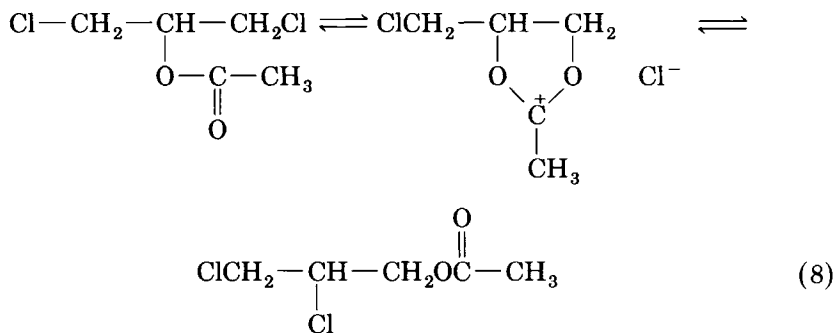
The new peak at 65.6 ppm (T) could be assigned to the CH_2OOC group of the branched product of eq. (5). If this was the case, the CHOOC — group of this product should show a change of its chemical shift, too. In the region 70–80 ppm, however, no other peak of similar intensity is detectable than the signal of the linear repeating unit. The peak at 54.7 ppm (D) is in a region

where $\text{CHCl} -$ groups absorb.⁹ But, with the exception of assuming a reversibility of eq. (5), the reactions described above do not show a possibility of forming a $\text{CHCl} -$ group.

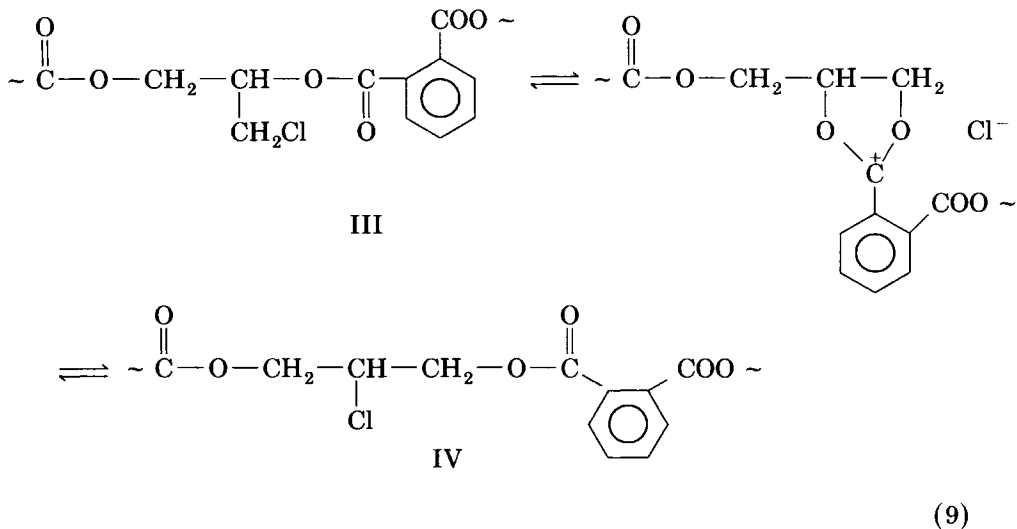
By looking for a more plausible explanation for the new NMR peaks, a reference was found which describes the thermal rearrangement of halohydrin acetates¹⁰



According to the authors, the dichloroacetate I rearranges when heated at 180°C to an equilibrium mixture of I (37%) and II (63%) in 9 h. Further experiments led to the conclusion that the rearrangement reaction proceeded via an actoxonium ion¹⁰:



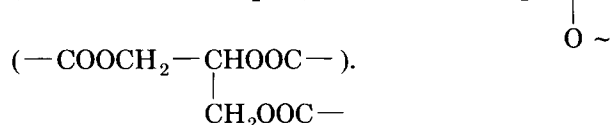
Structure I is very similar to the repeating unit of the epichlorohydrin-PSA-polyester III, and the corresponding rearrangement might be possible:



In structure IV, the Cl atom is bound to a secondary C atom which could explain the peak found at 54.7 ppm in the ^{13}C -NMR spectra [Fig. 2(b)]. The two CH_2O — groups are chemically equivalent and should give only one signal at 60–70 ppm, which, in fact, agrees with our results [65.5 ppm, Fig. 2(b)].

The ^1H -NMR spectra of structure II should have two peaks at ~ 4.1 ($\sim \text{CHCl}$) and ~ 4.4 ppm ($\text{CH}_2\text{OOC} \sim$).¹¹ As shown in Fig. 1(b), a shoulder at 4.5 ppm points to partial overlapping of these peaks with the peak at 4.6 ppm of the “normal” repeating unit. The changed peak areas of this spectrum correspond to a content of $\sim 25\%$ of structure IV and 75% of structure III, which is also in reasonable agreement with the relative peak intensities of the two peaks at 63.5 and 65.6 ppm of the ^{13}C -NMR spectra [Fig. 2(b)].

Thus, structure IV fully explains the changed NMR spectra of the high temperature product. As it is not a branched unit, it does, however, not contribute to the crosslinking process detected by GPC. Only the intermediate oxonium ion could be susceptible to an attack of the carboxylate or hydroxylate end groups and give the branched structures of eqs. (4) or (5). These branched structures and the possible new end group of eq. (6) must be present in concentrations of $< 10\%$ and may explain the small peaks at 73 ppm ($-\text{CH}-\text{O}-\text{CH}_2-$), 43 ppm ($\text{ClCH}_2-\text{CH}-\text{CH}_2\text{Cl}$), 64 and 71 ppm



As shown by Flory,¹² one crosslink by two polymer molecules is enough to cause the onset of infinite structures (gel), when chemical bonds between polymers are formed. Therefore, in our case, for a polymer with M_n of 8800 which is formed after 5 h at 100°C , about 1.5% of crosslinks would already be enough to build up an infinite network. This means that only the small quantities of side products, which are hardly detectable in the NMR spectra, cause crosslinking of the polymer, whereas the intense peaks which represent about 25% of the repeating units must be assigned to an isomer which does not contribute to branching, and is formed by the intramolecular rearrangement reaction of eq. (9).

Further experiments were carried out with 1-methylimidazole (1-MI) and tetraethylammonium bromide (TEAB) as catalysts, which gave similar results as in the case of the initiation with BDMA. At 100°C , linear polyesters were obtained with molecular weights (\bar{M}_n) of 4000–9000, whereas the reaction at 140 or 160°C afforded only partly soluble products with a very broad molecular weight distribution.

Copolymerization of Phenyl Glycidyl Ether and Phthalic Anhydride

The first experiments were carried out with PSA that was recrystallized once from toluene and still contained 0.2 mol % of acid. As Table II shows, the tertiary amines BDMA and 1-MI gave copolymers with \bar{M}_n of 6000–9000. Higher molecular weights of 14,000–17,000 were obtained by using the ammonium salts TEAB, TBAB, and TBAI. The molecular weight distribution was

TABLE II
 Copolymerization of PGE and PSA (1 : 1 mol/mol) with Tertiary Amines or Organic Salts
 as Initiators, PSA Containing 0.2 mol % of Acid

Initiator	Reaction conditions	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
0.3 mol % BDMA	5 h, 120°C	8900	11,800	1.3
0.3 mol % BDMA	5 h, 120°C + 24 h, 160°C	9400	13,300	1.4
1.2 mol % BDMA	5 h, 120°C	6400	7800	1.2
1.2 mol % BDMA	3 h, 140°C	6100	10,500	1.7
0.3 mol % 1-MI	5 h, 120°C	6800	16,100	2.4
0.3 mol % 1-MI	3 h, 140°C	6100	16,400	2.7
1.2 mol % 1-MI	5 h, 120°C	4300	10,300	2.4
1.2 mol % 1-MI	3 h, 140°C	5900	16,200	2.7
0.2 mol % TEAB	8 h, 140°C	17,000	23,900	1.4
1 mol % TEAB	5 h, 140°C	14,300	20,100	1.4
0.2 mol % TBAB	8 h, 140°C	14,000	49,200	3.5
0.2 mol % TBAI	8 h, 140°C	15,300	36,000	2.4

rather narrow with BDMA and TEAB as initiators, whereas TBAB yielded copolymers with a broader distribution of $\bar{M}_w/\bar{M}_n = 3.5$. Unlike the epichlorohydrin/PSA copolymers, no broadening of the molecular weight distribution was observed when the polymerizations were performed at 140 or 160°C.

More careful purification of the anhydride yielded copolymers of higher molecular weights. Surprisingly, the best result of $\bar{M}_n = 86,900$ was now obtained with 0.1 mol % of 1-MI as initiator. The initiation by 0.1 mol % of TEAB also gave high molecular weight copolymers ($\bar{M}_n = 69,000$) (Table III).

Catalyst concentrations of 0.05 mol % gave lower molecular weights with broader MW distribution. This indicates that this level was not enough to compensate impurities or some side reactions. TBAB and TBAI also yielded products with broader molecular weight distribution than the other catalysts

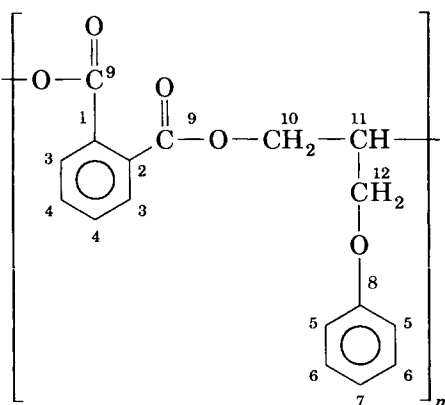
TABLE III
 Copolymerization of PGE and PSA (1 : 1 mol/mol) with Tertiary Amines
 and Ammonium Salts as Initiators, PSA Acid-Free^a

Initiator	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
0.05 mol % BDMA	20,800	56,300	2.7
0.1 mol % BDMA	27,800	51,400	1.8
0.2 mol % BDMA	26,000	46,600	1.8
0.05 mol % 1-MI	30,700	137,700	4.5
0.1 mol % 1-MI	86,900	149,100	1.7
0.2 mol % 1-MI	35,300	69,700	2.0
0.1 mol % TEAB	69,000	135,700	2.1
0.2 mol % TEAB	34,900	73,400	2.0
0.1 mol % TBAB	20,800	75,900	3.6
0.2 mol % TBAB	36,400	108,400	3.0
0.1 mol % TBAI	20,800	88,800	4.3
0.2 mol % TBAI	17,400	36,900	2.1

^a Reaction conditions 8 h, 140°C.

(Table III). With these salts chain transfer reactions are more likely to occur. I^- is a good "leaving group" and may readily be displaced by an alkoxide end group of another polymer chain. Thus, two polymer chains are connected by releasing the I^- , which can start a new shorter polymer chain. This leads to broadening of the MW distribution. TBAB gives a similar effect because the ion pair formed by this reagent is less tight than TEAB. The tetrabutyl allows easier displacement of Br^- or I^- than tetraethyl.

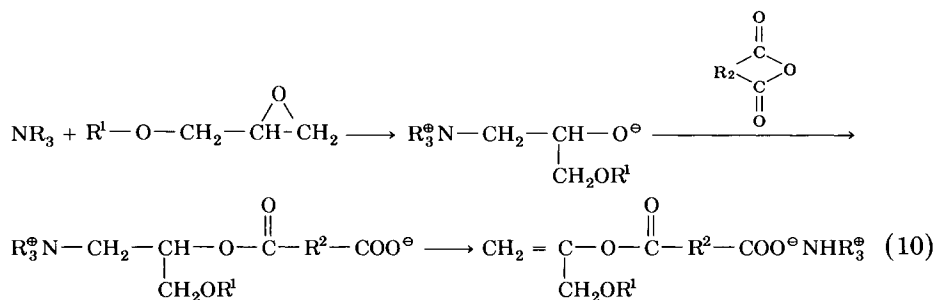
The products were amorphous white polymers with glass transitions of 60–68°C. The ^{13}C -NMR spectra show a quite distinct polyester structure (Fig. 3):



Ether groups from an epoxide homopolymerization cannot be detected, as there are no peaks between 74 and 78 ppm, where these groups should absorb.

By assuming a pure anionic mechanism with a fast initiation and without side reactions as described in (1) and (2), the expected degree of polymerization (\overline{DP}_n) can be calculated by the formula $\overline{DP}_n = [M_0]/[I_0]$.¹³ In our case, in the absence of impurities, initiator concentrations of 0.1 and 0.2 mol % should yield \overline{DP}_n of 1000 and 500, i.e., \overline{M}_n 149,000 and 74,500, respectively. As shown in Table III, such ideal results were not attained, the highest molecular weight of 86,900 being obtained with 0.1 mol % of 1-MI as initiator, which is 1.7 times less than the calculated value. Therefore, some transfer and termination reactions seem to occur even when thoroughly purified starting materials are used and extreme care is taken to avoid humidity.

For the tertiary amine catalyzed copolymerization, the following chain transfer reaction has been proposed by Fedtke and Domaratus¹⁴:



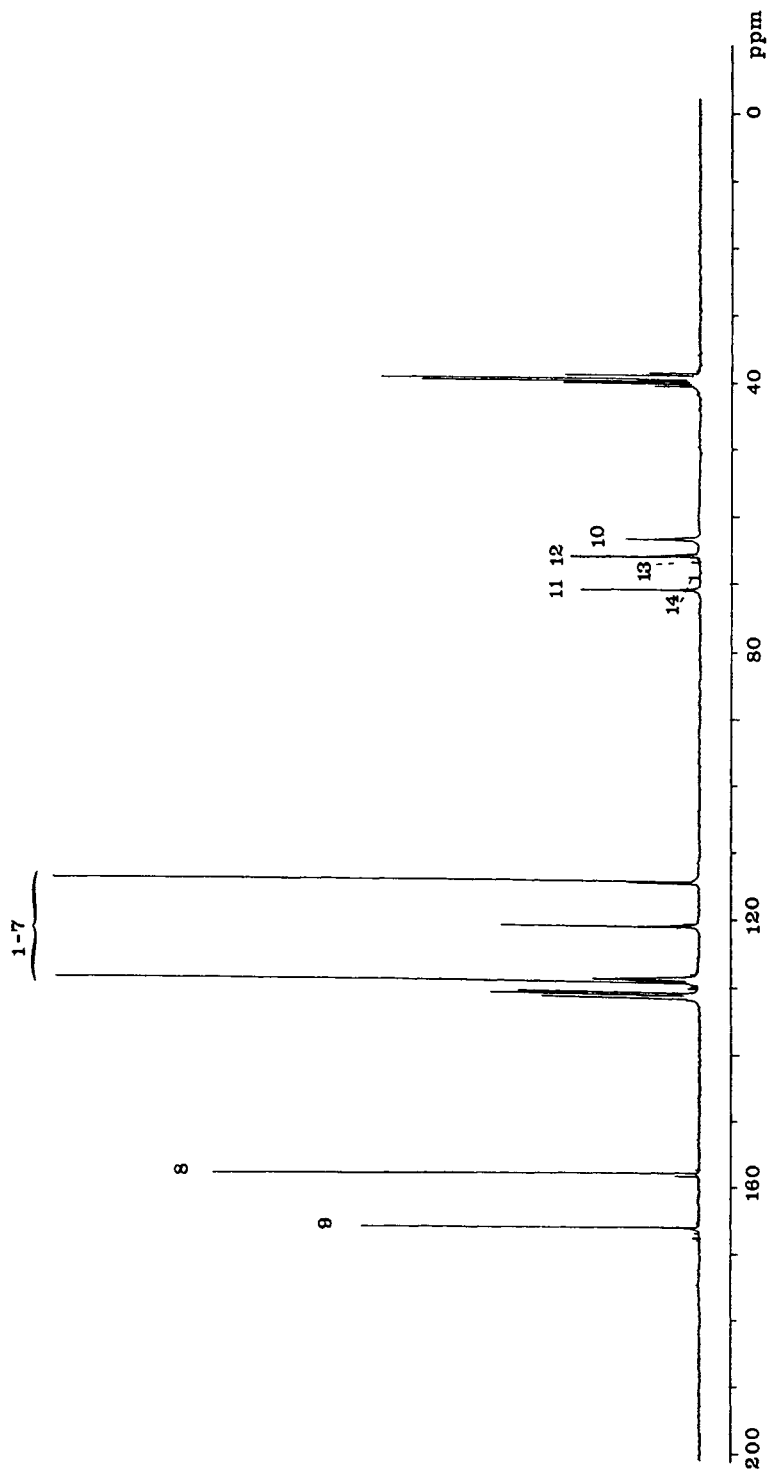
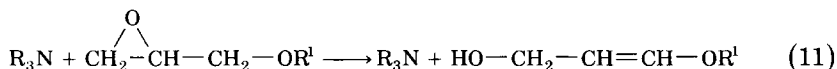


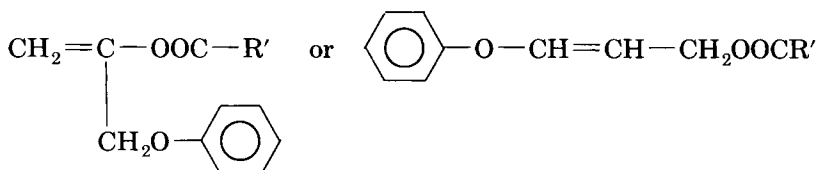
Fig. 3. ^{13}C -NMR spectrum of a PGE/PSA copolymer in DMSO- d_6 : initiation by 0.3% mol % 1-MI, \bar{M}_n 6800.

The reaction involves the release of the tertiary amine from the epoxide by formation of an ammonium ion and a double bond at the end of the polymer chain. Tanaka and Kakiuchi suggested a different initiation mechanism¹⁵:



In this reaction, the epoxide isomerizes spontaneously to an allyl alcohol under the influence of the tertiary amine. The allyl alcohol could start the polymerization by the reaction with an epoxide or an anhydride. Thus, the concentration of growing chains would be independent of the catalyst concentration and decrease the molecular weights of the resulting polymers.

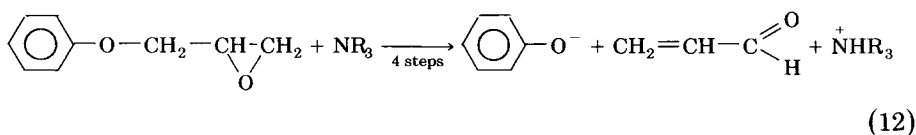
If one or both of these reactions occurred during the copolymerization of PGE and PSA, some characteristic peaks in the region 80–110 ppm should appear in the ¹³C-NMR spectra of the polymers, resulting from the polarized double bonds



In this region, the ¹³C-NMR spectra do not show any signals at all. Figure 3 shows a spectrum of a polyester with \bar{M}_n of 6800 recorded with 130,000 scans, a number which permits the detection of components in concentrations as low as 0.5%. Thus, the transfer or initiation reactions suggested in (5) and (6) have to be excluded for the PGE/PSA copolymerizations.

It has to be noticed, however, that, during each copolymerization experiment, some low molecular weight, colored impurities are formed, which are removed at the end of the reaction by repeated precipitations of the polyesters. GPC analysis of crude or not thoroughly purified products always shows about 2–5% of low molecular weight compounds which are responsible for low \bar{M}_n values and broad molecular weight distributions [Fig. 4(a)]. After purification of the products much higher \bar{M}_n values are obtained [Fig. 4(b)].

These low molecular weight impurities indicate that a cleavage reaction as described by Fedtke¹⁶ occurs. Fedtke found that PGE gives phenolate and acrolein in the presence of tertiary amines:



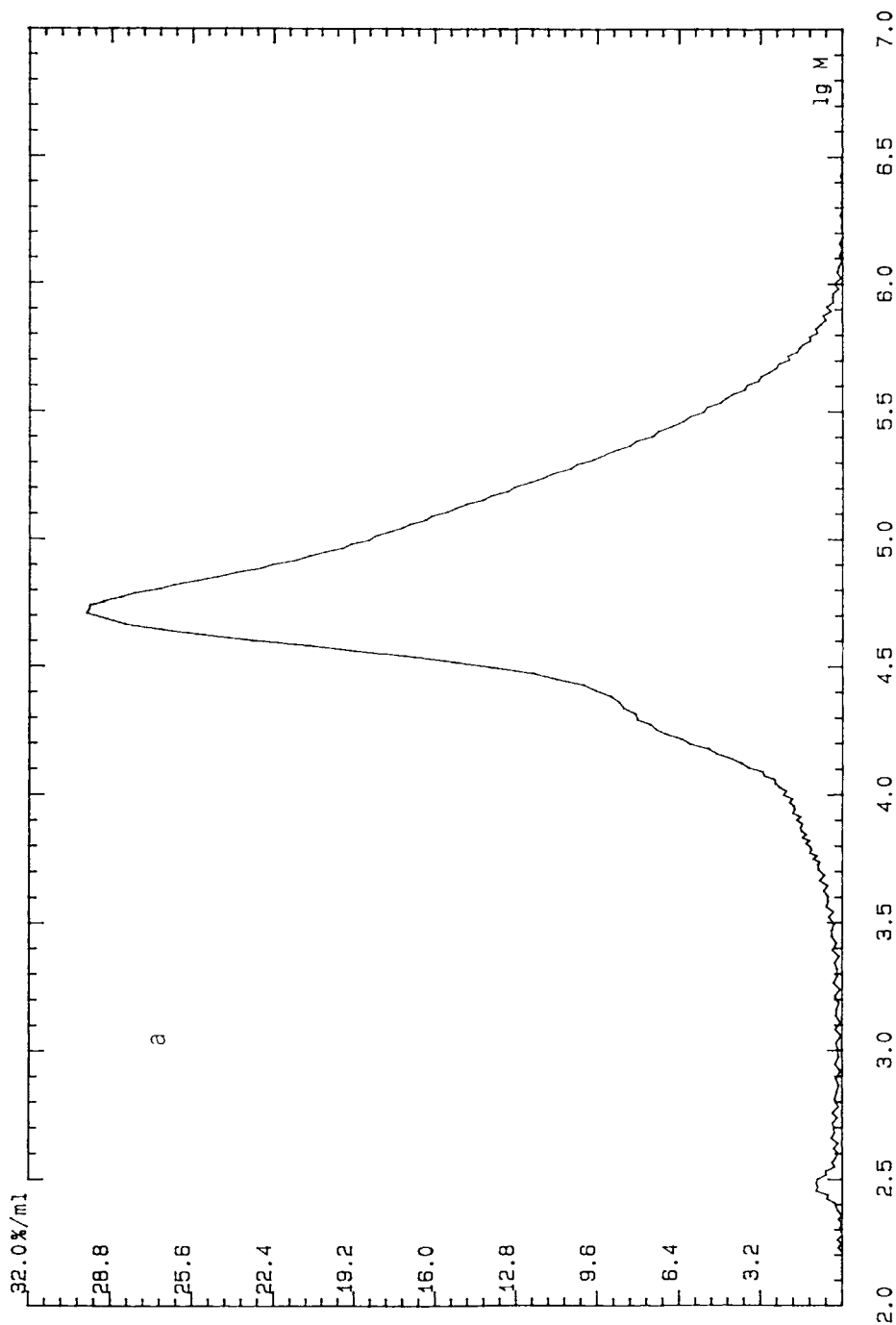


Fig. 4. GPC diagrams of a PGE/PSA copolymer initiated by TBAB: (a) crude product, $\bar{M}_n = 18,900$, $\bar{M}_w = 100,100$; (b) after reprecipitation from dichloroethane/ether, $\bar{M}_n = 36,400$, $\bar{M}_w = 108,400$.

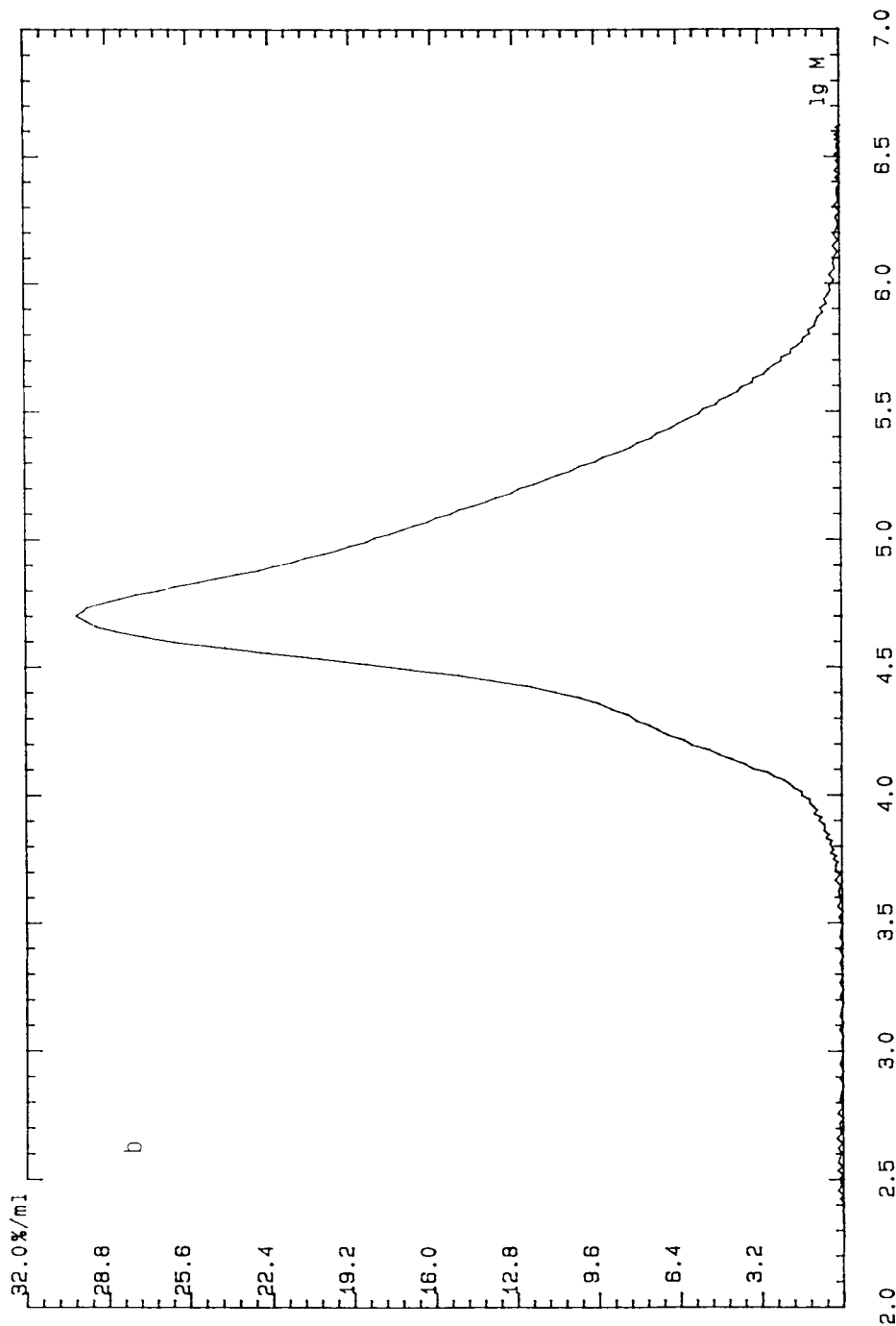
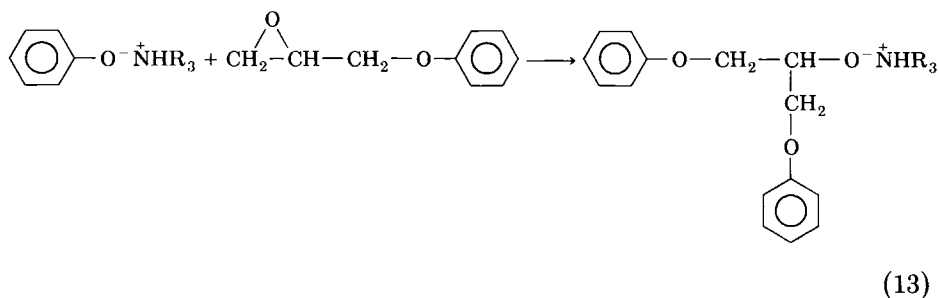
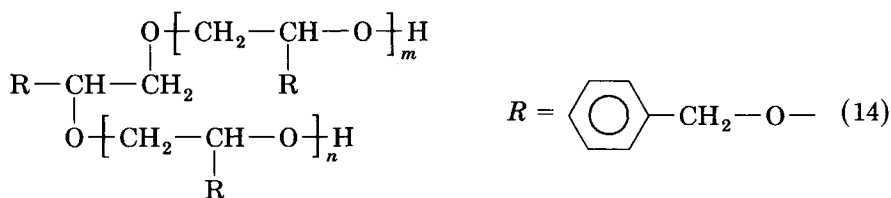


Fig. 4. (Continued from the previous page.)

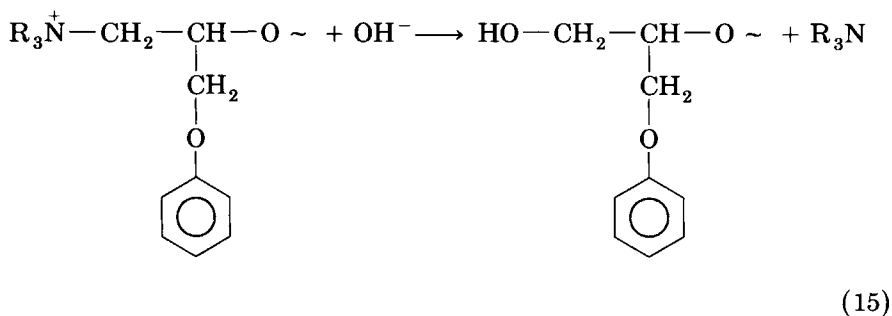
The phenolate then acts as new initiator by the following reaction:



In our case, acrolein and its possible reaction products with the monomers would be removed at the end of the reaction by the precipitation of the polymer. Besides this, Fedtke also found oligomers of the type

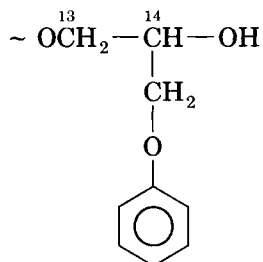


in the reaction mixture of PGE with BDMA or 1-MI. The mechanism which leads to the formation of these oligomers is not quite clear. It could, however, proceed easily by the reaction of an OH^- with the quaternary ammonium ion



The polymerization could then proceed in both directions and give a polymer with two hydroxyl end groups. The appearance of OH^- , of course, cannot be explained easily until now. The spectrum in Figure 3 only shows two additional peaks in the aliphatic region besides the signals of the "normal" polyester structure (at 65 and 69 ppm). These peaks can be assigned to

hydroxyl end groups of the form



An indication of carboxyl end groups is probably given by the very small peak at 168 ppm whereas the peak at 159 ppm (in the vicinity of 8) cannot be explained.

As no other end groups are detectable, it has to be assumed that structures as in eq. (13) or (14) are formed during the polymerization by the cleavage of PGE or some other side reaction. The starting group of eq. (13)



is so similar to the side group of the repeating unit that

it cannot be recognized by NMR spectroscopy. Polymers formed by the product of reaction (15) only have hydroxyl or carboxyl end groups, which agrees with the results presented here.

Curing of Bisphenol A Diglycidyl Ether (BADGE) with PSA

The question arose as to whether the results of the "model reactions" of monoepoxide and PSA can be transferred to the anhydride curing of epoxy resins, i.e., the crosslinking reaction of BADGE with PSA, catalyzed by the same amines and ammonium salts as above; would the properties of the crosslinked products reflect the differences of molecular weights obtained by the use of more or less pure PSA and different catalysts or are there other factors which determine the final properties of the products?

The parameter which is used to characterize a polymer network is the crosslink density which is the reciprocal value of the average molecular weight between crosslinks. In crosslinked polymers formed by the reaction of identical monomers, but initiated by different catalysts as in our case, variations in crosslink density are only caused by differences in end-group concentration of the resulting product, i.e., the number of defects in the network. As found by several authors,¹⁷⁻¹⁹ the crosslink density ($1/M_c$) is proportional to the glass transition temperature T_g . Thus, if linear copolymerization and crosslinking reaction obey the same mechanisms, the T_g values of the crosslinked polymers should depend on the type and concentration of the catalyst and on the purity of starting materials in the same way as the molecular weights of the model compounds.

Table IV shows the results of a series of curing experiments with different initiators and the two qualities of PSA. The highest T_g values are obtained with 0.1 mol % of initiator. Exceptions are TBAB and TBAI which in two

TABLE IV
 T_g Ranges of BADGE/PSA Networks^a

Initiator	Concentrations (mol %)	T_g range (°C) ^b	T_g range (°C) ^c
BDMA	0.05	103–138	
	0.1	148–157	136–154
	0.2	139–150	
1-MI	0.05	112–160	
	0.1	143–159	155–168
	0.2	142–156	
TEAB	0.05	120–166	148–162
	0.1	160–170	149–167
	0.2	155–172	
TBAB	0.05	152–165	152–165
	0.1	109–134	155–164
	0.2	71–155	
TBAI	0.05	150–167	145–159
	0.1	153–167	134–147
	0.2	50–150	

^a Curing condition: 140°C, 15 h (T_g values of second DSC run, both runs 20–250°C, 10°C/min).

^b PSA containing 0.2 mol % acid.

^c PSA acid free.

cases yield better results with 0.05 mol % of initiator. For the series of curing experiments with “impure” PSA, when only the optimum T_g values for each catalyst are considered, glass transitions show the same dependence on the initiator type as the molecular weights (\bar{M}_n) of the model compounds. The PGE/PSA copolymerization yields the highest molecular weights (by using impure PSA) with TEAB as initiator, followed by the other two ammonium salts. The highest T_g 's of the BADGE-PSA curing are also obtained with TEAB, TBAI, and TBAB.

Surprising effects are, however, observed, when pure, acid-free PSA is used which caused such a dramatic increase in molecular weights in the case of the PGE/PSA-copolymerizations. As shown in Table IV, with the exception of 1-MI and TBAB, glass transitions are lower for the acid-free than for the acid-containing PSA curing. The 1-MI-initiated product has the highest T_g in this series which would correspond to the highest \bar{M}_n obtained in the model reaction. The decreasing T_g 's in the order TBAB, TEAB, TBAI, and BDMA, however, do not correlate with the molecular weights of the PGE/PSA copolymers. In addition, the highest glass transition obtained under “pure” conditions is inferior to the highest T_g of the curing with acid-containing PSA.

How can these results be interpreted? Apparently, crosslink density is not only a function of molecular weights, which, for an anionic polymerization mechanism, depend on the catalyst concentration, the purity of the monomers and the presence of side reactions. As gelation occurs very early in these systems (at conversions of about 20% of epoxide groups), physical effects seem to play an equally important role in the network formation. Several authors^{20–22} report that cured epoxies contain regions of heterogenous crosslink density. Ordered regions have been described as agglomerates of colloidal particles in a lower molecular weight interstitial fluid.²³ Salomon et al.²⁴ suggested that a two-phase system is produced by microgelation prior

to the formation of a macrogel. These observations indicate that the crosslinking reaction does not lead to an ideal, regular network. The formation of a very dense network by the reaction of a four-functional diepoxide with a difunctional anhydride as in our case, which causes an early gelation, makes it unlikely that all the functional groups can meet and react with each other. Furthermore, microgelation and formation of a macrogel, must occur sooner (i.e., at lower conversions) the higher the initial molecular weights of the growing polymers. Thus, the formation of high molecular weight polymers, which would increase the crosslink density under ideal conditions, has also the contrary effect of an earlier gel formation, and the buildup of more defectuous, inhomogenous products.

These phenomena could explain the unexpected results of obtaining lower glass transitions under conditions which lead to higher molecular weight products in the case of a linear copolymerization.

CONCLUSIONS

These investigations have shown that it is possible to prepare regular alternating copolymers from phenyl glycidyl ether and phthalic anhydride with molecular weights up to 87,000 and with rather narrow molecular weight distributions by using simple tertiary amines or ammonium salts as catalysts. As for every anionic polymerization, it is necessary to work under conditions of high purity to reach this objective. Deviations from the calculated molecular weights are possibly caused by a cleavage reaction of the monomer in the presence of tertiary amines as described by Fedtke.¹⁶ The formation of double bonds by mechanisms suggested by Fedtke and Domaratius¹⁴ or Tanaka and Kakiuchi¹⁵ was not observed for these copolymerizations.

For the understanding of the crosslinking reaction of diepoxides with anhydrides, it is, however, not sufficient to know the influence of monomer purity and of initiator type and concentration on the molecular weights of model compounds. As glass transitions of the products from the crosslinking reaction of BADGE with PSA do not correlate with the molecular weights of the linear copolymers from PGE and PSA obtained under similar conditions, other factors also seem to influence the final crosslink density of the products.

Evidently, no regular networks are built up when the monomeric four-functional diepoxide used for these investigations reacts with a difunctional anhydride. Micro- and macrogelation occur so early that not all the functional groups can react and defectuous heterogenous products are formed. The higher the molecular weights of the growing polymers at the beginning of the reaction, the more pronounced these effects must be. More detailed studies are necessary to understand these aspects of the anhydride curing of epoxides.

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