Macromolecules **1980**, *13*, 377–380

Linear Polybenzyls. 4. Effect of Nitroethane on the Polymerization of α-Chloroethylbenzene

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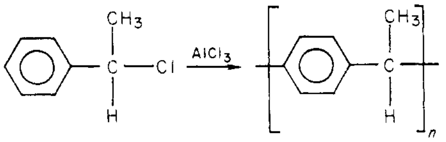
ABSTRACT: Poly(α-methylbenzyl) was prepared by the Friedel–Crafts polycondensation of α-chloroethylbenzene at reaction temperatures varying from −125 to −78 °C with $AlCl_3$ as the catalyst. Polymers prepared at −125 °C in ethyl chloride possessed high linearity and stereoregularity and accordingly also showed relatively high crystallinity, while polymers prepared at temperatures above −100 °C had increasingly lower stereoregularities. However, when the polymerization was carried out at −65 °C in the presence of nitroethane, the resulting polymers showed no loss in linearity or stereoregularity. Higher yields and higher molecular weights were also obtained under these conditions than at −125 °C in the absence of nitroethane. The ratio of the nitroethane to $AlCl_3$ was optimized by investigating the model compound reaction of α-chloroethylbenzene with α,α-diphenylethane.

Previous investigations have shown that poly(α-methylbenzyl) can possess significant linearity, stereoregularity, and crystallinity when prepared under certain reaction conditions.[1-5] The crystallinity in this polymer has been attributed to the high degree of para substitution and isotacticity apparently resulting from the steric effects of the methyl group attached to the benzyl carbon, eq 1.



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Polymer samples having the highest crystallinity and molecular weight were prepared from α-chloroethylbenzene, using $AlCl_3$ as the catalyst at a reaction temperature of −125 °C.[4] In these reactions polymer yields and molecular weights were found to vary with the monomer-to-catalyst ratio. However, the reproducibility of the properties of the products was poor, possibly because of either the low solubility of $AlCl_3$ or of the presence of impurities or difficulties in constantly maintaining very low reaction temperatures.

The objective of the present investigation was to study the effect of nitroethane on the polymerization of α-chloroethylbenzene by comparing the polymer structure and properties so obtained with those of polymers prepared in the absence of this reagent.[9]

It was expected that nitroethane would modify the catalytic activity of $AlCl_3$ by forming a soluble complex, which would give more reproducible results and a higher positional selectivity at reaction temperatures above −125 °C. It has previously been shown that at temperatures above −125 °C, the $AlCl_3$-catalyzed polymerization reactions yielded increasingly noncrystalline polymers.[4]

Experimental Section

Solvents. Ethyl chloride and methyl chloride gases were purified by passage through a 2-ft column packed with potassium hydroxide, anhydrous calcium chloride, anhydrous calcium sulfate, and molecular sieves (3 Å) before being condensed directly into reaction flasks at −78 °C. Nitroethane was dried over anhydrous calcium chloride and distilled through a column packed with glass helices. The fraction of nitroethane with a boiling point range of 114–116 °C was collected and stored over fresh, anhydrous calcium chloride under an atmosphere of dry nitrogen. Reagent grade tetrahydrofuran was distilled over lithium aluminum hydride.

Table I
Model Compound Reactions of α-Chloroethylbenzene with α,α-Diphenylethane at −65 °C[a]

	substitution distribution, %		
$EtNO_2:AlCl_3$[b]	para	ortho	meta
0.00	90.6	0.8	8.6
0.52	91.3	0.0	8.7
1.04	82.5	0.0	17.5
2.08	94.3	0.0	5.7
4.16	98.4	0.0	1.6
5.20	100.0	0.0	0.0
6.24	100.0	0.0	0.0

[a] For a 60-min reaction time in ethyl chloride. [b] Mole ratio of nitroethane to $AlCl_3$.

Catalyst. Anhydrous $AlCl_3$ was sublimed repeatedly at 20 mmHg until white crystals were obtained.

Monomers. α-Chloroethylbenzene (Eastman Kodak Co.) was fractionally distilled through a 16-in. column packed with glass helices. The pressure was reduced to 0.6–0.8 mmHg before heat was applied. When degassing of the liquid was completed, the monomer was heated and the fraction collected at 29–30 °C was stored under vacuum and kept at −10 °C until needed. Just before use, the stored monomer was analyzed by gas chromatography (GC) at 80 °C and found to be 99.9+% pure. GC analysis at higher temperatures resulted in dehydrochlorination.

Reaction Systems. The all glass reaction system used in the model compound and polymerization reactions was dried overnight at 170 °C and assembled while still hot. Rubber septa were used to seal the reaction system, which was purged with dry nitrogen gas, and during the reaction a constant flow of dry nitrogen was maintained through the system.

Model Reactions. Samples of *o*-, and *m*-, and *p*-bis(α-phenylethyl)benzene were prepared by reacting α-chloroethylbenzene with excess α,α-diphenylethane at −65 °C in ethyl chloride, using the ratios of nitroethane-to-$AlCl_3$ listed in Table I. The reactions were terminated by pouring the solutions into excess methanol. α,α-Diphenylethane was prepared according to the method of Kuo and Lenz[4] by the hydrogenation of α,α-diphenylethylene (Eastman Kodak Co.). GC, IR, and NMR analyses were used to characterize the structure and purity of the hydrogenated product. Isomer distributions of bis(α-phenylethyl)benzene from the model reactions were analyzed by GC, using the procedure of Kuo and Lenz.[4]

Polymerization of α-Chloroethylbenzene. Conditions used for the polymerization of α-chloroethylbenzene are listed in Table II. The general polymerization procedure was as follows: in a dry bag, $AlCl_3$ was placed in a 150-mL Schlenk tube, which was

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0024-9297/80/2213-0377$01.00/0

Table II
Polymerization Conditions and Polymer Properties

react. conditions[a]		$[M]/[AlCl_3]$[b]	$[EtNO_2]/[AlCl_3]$[c]	yield, %	polymer properties				
temp, °C	time, h				$\overline{DP}_n$[d]	I[e]	T_m, °C[f]	$\overline{M}_w/\overline{M}_n$[d]	T_g, °C[f]
-78	4.5	6.1		72	16	0.68	112	1.8	
-93	5	5.3		60	130[g]			1.5	
						0.84	169		96
					24[g]			1.9	
-108	4	3		95	121	0.94	167	4.6	80
-125	2.8	2.7		70	15	0.81	160	1.8	80
	5	3.0		95	23	0.80	178	3.0	90
	10	19		40	11	0.87	142	1.9	99
	10.3	28		83	13	0.87	151	2.8	96
	103	13		83	23	0.73	128	2.2	75
-65	20.5	4.1	6.7	100	82	0.89	229	1.7[h]	103
	48	3.1	4.2	100	12	0.76	129	2.1	72
	40.5	2.2	6.3	90	20	0.43	128	3.9	75
	90	3.0	6.3	100	20	0.87	222	2.3[h]	82
	108.5	3.5	6.3	100	39	0.90	250	2.3[h]	95

[a] The reaction solvent was ethyl chloride. [b] Mole ratio of monomer to $AlCl_3$. [c] Mole ratio of nitroethane to $AlCl_3$. [d] Weight and number average molecular weights ($\overline{M}_w$ and $\overline{M}_n$, respectively) were determined by GPC relative to polystyrene as the standard. [e] Fraction of isotactic triads as determined by ^1H NMR. [f] As measured by DSC. [g] From analysis of bimodal distribution in the GPC plot of Figure 1. [h] The GPC distribution curve contained a shoulder.

sealed with a rubber septum, 100 mL of purified ethyl chloride gas was condensed into the tube at -78 °C, and the mixture was stored at that temperature under a blanket of dry nitrogen gas. Where required, the addition of nitroethane to the $AlCl_3$ solution was made at this time, from a syringe. Approximately 100 mL of ethyl chloride was condensed at -78 °C into a nitrogen-purged, 300-mL, three-neck, round-bottom flask equipped with a mechanical stirrer and sealed from the atmosphere with rubber septa. α-Chloroethylbenzene was added from a syringe while the flask was maintained at -78 °C under dry nitrogen. The two flasks containing the catalyst and monomer solutions, maintained at -78 °C under a dry nitrogen atmosphere, were connected to each other with Teflon tubing inserted through the septa. Both solutions were brought to the desired reaction temperature and equilibrated for 15 min. The $AlCl_3$ solution was then pumped through the Teflon tube into the monomer solution under nitrogen gas pressure. The catalyst solution was added over a 1-h period, and a color change from clear light yellow to bright orange or red was observed. The reaction was terminated after a specified time by pouring the cold solution into 2 L of vigorously stirred cold methanol. The reaction products were analyzed by NMR, IR, GPC, and DSC.

Polymer Characterization. Molecular weights and molecular weight distributions were determined using a Waters Associates high-pressure liquid chromatograph equipped with Styrogel columns and based on polystyrene as the standard. Tetrahydrofuran was used as the solvent at room temperature. ^1H NMR spectra were recorded on a Perkin-Elmer R32 90-MHz spectrometer and IR spectra on a Perkin-Elmer spectrometer, Model 257. TGA thermograms were obtained with a DuPont analyzer and DSC thermograms with a Perkin-Elmer DSC, Models 1B and 2. GC analyses were carried out on a Varian aerograph gas chromatograph, Model 1520.

Results and Discussion

The polymerization of α-chloroethylbenzene is a step-growth, condensation polymerization reaction involving a Friedel–Crafts aromatic alkylation. Previous investigations in this laboratory have found that the most effective catalyst for this reaction is $AlCl_3$,[4] but this catalyst can only be used to prepare crystalline polymers at temperatures below -80 °C. In addition, the products from these polymerization reactions were quite variable in properties and were difficult to reproduce. This behavior is consistent with previous reports of the variability in the catalytic behavior of $AlCl_3$ and its tendency to cause undesirable side reactions.[6,7] Previous workers have found it necessary to use a large excess of this catalyst in the polymerization of benzyl chloride possibly for this reason.

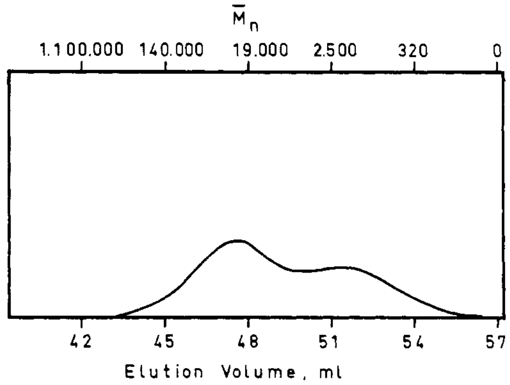


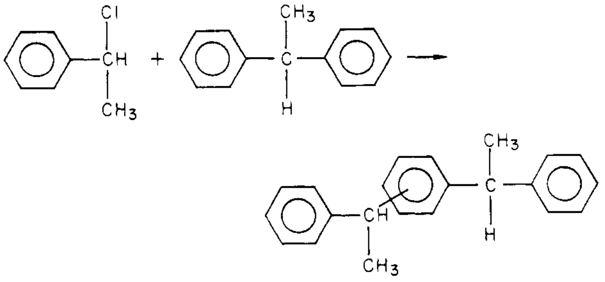
Figure 1. Molecular weight distribution by GPC of the bimodal polymer in Table II (footnote *g*).

Another problem in the use of $AlCl_3$ is its low degree of solubility in many of the solvents which are desirable for use in Friedel–Crafts reactions, particularly at low temperature. Although $AlCl_3$ is soluble in ethers, ketones, and alcohols, the resulting solutions in these solvents have very low or no activity in alkylation reactions. On the other hand, nitro compounds have been found to be effective solvents in some Friedel–Crafts reactions, so the present investigation was concerned with the use of these compounds as complexing agents to increase the solubility of $AlCl_3$ in ethyl chloride.[6,8,9]

Nitro compounds in general are good solvents for $AlCl_3$, and equimolar addition complexes of nitro compounds and $AlCl_3$ have been isolated and found to be catalytically active.[6] In certain reactions where the ring positions on the aromatic substrate are sterically hindered, a nitrobenzene–$AlCl_3$ catalyst has been shown to promote higher selectivity for the least hindered positions than for the uncomplexed $AlCl_3$.[8] However, in the few cases where nitromethane has been used in the polycondensation of α-chloroethylbenzene, only highly branched polymers were obtained.[4,10] The probable explanation for this contradiction is that the reaction temperatures used in those polymerizations were too high. Higher temperatures are known to increase greatly catalytic activity and would be expected to reduce the effect of steric contributions of the methyl group on the benzyl carbon resulting in higher degrees of alkylation at the ortho and meta positions. Information based on other reactions suggests that low temperatures should decrease the catalytic activity and increase the selectivity of the nitro compound-$AlCl_3$ system.[10]

To take advantage of the more soluble complexes formed between $AlCl_3$ and nitro compounds and of the selectivity provided by the low reaction temperatures, the nitro compound was added to a reaction carried out in solution in ethyl chloride. Three common nitro compounds which are often used for Friedel-Crafts reactions are nitrobenzene, nitromethane, and nitroethane. These have freezing points of 9, −17, and −50 °C, respectively, so nitroethane was chosen for these investigations although the other two were also evaluated with similar results.

Model Reaction. A model reaction of α-chloroethylbenzene with α,α-diphenylethane, shown in eq 2, was first



(2)

investigated to determine the optimum nitroethane-to-$AlCl_3$ ratio, and data on the isomer distributions obtained in this reaction are given in Table I. The results indicate that a ratio of between 5.2 and 6.2 of nitroethane-to-$AlCl_3$ is preferred for the preparation of para-substituted bis(α-phenylethyl)benzene, so a ratio slightly in excess of 6 was used for most polymerization ractions. The reaction temperature of −65 °C was chosen because preliminary polymerization reaction studies showed very little catalytic activity for the nitroethane-$AlCl_3$ complex below −70 °C.

Polymerization Reactions. The results for the polymerization reactions carried out in the presence and absence of nitroethane (as a complexing agent for the $AlCl_3$ catalyst) are collected in Table II. The principal advantage of the use of this complexing agent was in its ability to allow us to carry out the polymerization reaction at a much higher temperature in ethyl chloride (−65 °C compared to −125 °C in the absence of nitroethane) and still obtain the linear and crystalline polymer. In addition, quantitative yields of polymer were obtained in almost all cases with the use of the complexed catalyst at the higher temperature, while the products from polymerization reactions with the uncomplexed catalyst in the same solvent at lower temperature were obtained in yields varying from 40–95% with little or no predictability. Furthermore, the use of the complexed catalyst gave, in general, polymers of higher molecular weight and higher melting points.

A number of important observations and conclusions can be made from the data in Table II about the interrelationships between the reaction parameters and the polymer properties, including the following:

(1) In many products bimodal molecular weight distributions were observed on analysis by gel permeation chromatography, GPC. A particularly important example is shown in Figure 1 for the polymer obtained at −93 °C in the absence of nitroethane. The approximate values for $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ for each of the two peaks in this chromatogram are given in Table II. The cause of the formation of two peaks, which is certainly unusual for a step-growth or condensation polymerization reaction, is unknown but may be related to the same phenomenon observed in the closely-related cationic polymerization reactions of styrene.[11] In that case, the formation of a bimodal distribution was attributed to the presence of two different types of active species (carbenium ion pairs) in the propagation reaction.

(2) In the absence of nitroethane, the polymer obtained at −78 °C had a very low tacticity and melting point. The same result was observed at −65 °C when apparently an insufficient amount of complexing agent was used (4.2 mol of nitroethane per mol of $AlCl_3$) so that not all of the catalyst was complexed. A polymer of very low tacticity and melting point was also obtained when the ratio of monomer-to-catalyst was too low (2.2:1), and a ratio of at least 3:1 was needed to form a polymer with high stereoregularity. The 2.2:1 polymer also had a broad bimodal distribution compared to the expected most-probable distributions of the other polymers in this series, although several of these showed the presence of a shoulder in the distribution curves as indicated in Table II.

(3) All results indicate that longer reaction times do not necessarily lead to higher molecular weights and indeed the reverse may be true. It is conceivable that, during long reaction times, dealkylation may occur resulting in polymer chain scission and a reduced molecular weight.

(4) It is to be expected that both molecular weight and tacticity will control the melting points, T_m, and the glass temperature, T_g, of the polymers formed. In general, these effects are observed in the data in Table II with both T_m and T_g increasing with increasing isotactic triad content and $\bar{M}_n$.

Polymer Structures and Properties. In an earlier report from this laboratory, the minor peak at δ 7.15 in the phenylene region of the ^{1}H NMR spectrum was assumed to be an indication of branching. Very recent investigations strongly suggest that this peak is derived from a nonisotactic triad in the polymer.[12] Based on this assignment, the results listed in Table II for isotactic triad contents of the polymers were calculated from the relative peak areas at δ 7.04 and 7.15. This ratio was in good agreement with the melting points observed, as discussed above, when taking into account the expected decrease in melting point with decreasing molecular weight. However, it is surprising that a melting endotherm was observed in the polymer sample in Table II which had a degree of isotacticity of only 0.43 as determined in this way.

The melting points reported in Table II were obtained on the polymers isolated directly from the reaction mixture without annealing, and the values for the polymers obtained from reactions in which nitroethane was used were unusually high.[4] The melting point of 250 °C for the last polymer in Table II is the highest ever observed in this laboratory. In general, the glass temperatures were also slightly higher but very similar to those previously reported for poly(α-methylbenzyl).[4]

Acknowledgment. The authors are grateful to the Exxon Chemical Co., Plastics Technology Division, for the support of this work and to the NSF-sponsored Materials Research Laboratory at the University of Massachusetts for the use of its facilities.

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Nonlinear Viscoelasticity of Concentrated Polymeric Liquids

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Received August 8, 1979

ABSTRACT: Following Doi and Edwards, the topological constraints imposed on a polymer molecule by surrounding molecules are described by means of a harmonic potential which confines the molecule in a "tube" of a certain radius. In reviewing this theory, a number of equations are rederived by a different method. The result of the calculation defines the free energy of the molecule in the tube and this leads in a straightforward manner to the tensile force in the molecule and to the lateral pressure exerted by it. In contrast to the assumption made by Doi and Edwards, it is assumed that a deformation of the system gives rise to a new tube radius. Its magnitude is determined by the equilibrium between the lateral pressure exerted by the molecule and the elastic response of the surrounding medium. This model gives results that are intermediate between the extreme cases of constant tube radius assumed by Doi and Edwards and constant segment volume assumed by Marrucci and de Cindio. It depends on the constitutive properties of the system which one of the limits is approached. Moreover, the model explains in a natural way the experimentally observed maximum in plots of elongational viscosity vs. stretching rate.

The nonlinear viscoelastic behavior of concentrated polymeric liquids, either melts or solutions, has long been described by the use of a strict analogy with the classical theory of rubber-like elasticity. Instead of permanent junction points of the chain network made by the chemical cross-links, impermanent junctions due to entanglements were supposed. The chains of the network were assumed to follow affinely the external deformation, and only the renewal rate of the impermanent junctions remained to be established. By taking a constant renewal rate, Lodge[1] derived the following equation for the stress tensor

$$\sigma = \int_{-\infty}^{t} \mathbf{C}_t^{-1}(t')\mu'(t - t')\, \mathrm{d}t' \qquad (1)$$

where $\mathbf{C}_t(t')$ is the "history" of the Cauchy deformation tensor and μ' is called the memory function.

Subsequent modifications of Lodge's theory, by the use of different assumptions on the rate of junction renewal, gave rise to equations similar to eq 1 but with a different memory function, which also depended on some scalar measure of the deformation history. In any case, the tensorial form of the stress tensor was dictated by $\mathbf{C}^{-1}$, which is a consequence of the assumption of affine deformation.

A novel approach was recently taken by Doi and Edwards[2-5] on the basis of the "reptation" idea of de Gennes.[6] The fundamental assumption is that long linear flexible macromolecules in concentrated systems can only diffuse along their own length, the lateral movements being effectively hindered by the topological constraints made by the other chains. With appropriate additional assumptions, Doi and Edwards derived the following constitutive equation

$$\sigma = \int_{-\infty}^{t} \mathbf{Q}_t(t')\mu'(t - t')\, \mathrm{d}t' \qquad (2)$$

where $\mathbf{Q}$ is a tensor quite different from $\mathbf{C}^{-1}$.

Equation 2 shows many interesting features which are at variance with those derived by means of eq 1. For example, in a shear flow the tensor $\mathbf{Q}$ predicts a nonzero negative value for the second normal stress difference, in agreement with experiments, while the tensor $\mathbf{C}^{-1}$ gives zero for that quantity. Also, eq 2 "naturally" predicts a shear rate dependent viscosity while in order to obtain the same result from eq 1 it is necessary to adopt a memory function which, in one way or another, depends on the deformation history.

Although the approach used by Doi and Edwards is undoubtly sound and the general picture of the physics involved is extremely appealing, it appears that one of the assumptions made in the derivation is open to question. The matter has already been considered in a recent paper[7] where it is shown that the relaxation behavior of a molten polymer at high extensions agrees better with a variant of the theory which was obtained in ref 7 by modifying the assumption in question. On the other hand, relaxation data obtained in concentrated solutions[8] seem to agree much better with the predictions by Doi and Edwards.[3]

In this paper we shall further examine this matter and offer a possible solution. The motivations for this analysis are briefly indicated as follows. In the first place, the assumption made in ref 3 is in itself a doubtful one, for which the authors themselves develop only a "plausible" argument. At first sight, the alternative advanced in ref 7 looks more consistent with the overall model but, when carefully inspected, it also presents nonnegligible difficulties. Second, either assumption leads to results which should apply universally, i.e., independently of any characteristics of the particular system, whereas the actual behavior of different concentrated polymeric liquids indicates that differences, even qualitative ones, indeed exist. Finally, some of the predictions of the theory by Doi and Edwards appear unsatisfactory. We refer in particular to the behavior in elongational flow which is considered in ref 5. It is there predicted that the elongational viscosity

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0024-9297/80/2213-0380$01.00/0