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Polymerization of α-Ethylbenzyl Chloride

Linear Polybenzyls V.

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SUMMARY

α-Ethylbenzyl chloride was polymerized at -100° in ethylchloride with $AlCl_3$ catalyst. The polymer obtained was crystalline with a melting point at about 95°C. A maximum degree of polymerization of approximately 80 was achieved within one hour, and longer reaction times caused a decrease in molecular weight and a narrowing of the molecular weight distribution. NMR analysis indicated that the polymer is highly stereoregular and, in analogy to poly-α-methylbenzyl, most likely isotactic.

INTRODUCTION

Previous investigations in this laboratory have been concerned with the effects of catalyst, solvent, temperature and monomer structure on the Friedel-Crafts polymerization of benzyl chloride and substituted benzyl chlorides[1-4]. It was observed that polymer linearity was strongly effected by the presence of substituents on either the benzyl carbon atom or the aromatic ring. Benzyl chloride gave branched polymers even at polymerization temperatures below -120°C, but α-methylbenzyl chloride could be polymerized to linear, crystalline polymers at reaction temperatures as high as -65°C[4] under the proper conditions. It was of interest, therefore, to evaluate the effect of larger substituents at the α-position on both the polymerization reaction and the properties of the resulting polymers, and a series of α-alkylbenzyl chlorides has been prepared for this purpose. The present report is concerned

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with the polymerization of α-ethylbenzyl chloride. Work now in progress on α-isopropyl- and α-t-butylbenzyl chloride will be described in the future.

Kennedy and Isaacson [5] were the first to prepare crystalline polymers by the Friedel-Crafts polymerization reactions of both benzyl chloride and α-methylbenzylchloride at low temperatures (-130°C). However, Montaudo and coworkers [6] reported that the polymer from benzyl chloride was crystalline only after careful fractionation of a polymer sample obtained at low conversion. Much higher crystallinities were observed in the polymer from α-methylbenzyl chloride, and it was concluded from X-ray diffraction studies [1] that the polymer was isotactic. Melting points as high as 250°C have been observed for this polymer [4]. In the present work, α-ethylbenzyl chloride was polymerized in the same solvent, ethyl chloride, with the same catalyst, aluminium chloride, as used for the α-methyl monomer at a reaction temperature of -100°C to compare the structures and properties of the two polymers.

EXPERIMENTAL

α-Ethylbenzyl chloride was prepared by the reaction of α-ethylbenzyl carbinol (Aldrich) with dry HCl gas at 0°C [6]. The product was isolated, washed, dried and distilled in vacuum; bp (0.5 Torr): 45-47°C; Yield: 71 %; Anal.: calcd., C, 69.90; H, 7.17; Cl, 22.93; Found, C, 70.03; H, 6.87; Cl, 22.79. The crude monomer was carefully fractionated by vacuum distillation and stored under nitrogen at -30°C. Analyses by gas chromatography showed no impurity present (2 m 5 % Carbowax column, injection temp.: 70°C, detector: 200°C) so the purity was assumed to be better than 99.5 %.

The catalyst ($AlCl_3$, Aldrich) was freshly sublimated before used. All polymerization reactions were performed at -100°C in ethyl chloride as solvent. The reaction mixture was maintained under a constant flow of dry nitrogen as described elsewhere [7]. The polymer obtained was washed with methanol and dried in vacuum at 50°C. Anal.: Calcd. C, 91.47; H, 8.53; Found, C, 90.06, 91.92; H, 8.15, 8.59. Molecular weights and molecular weight distributions were determined on a Waters Associates HPLC, Model 501 with Styrogel columns and tetrahydrofuran as the solvent. Crystalline properties were measured on a Perkin-Elmer DSC1B at a heating rate of 20°C/min. NMR spectra were obtained on either a Bruker 270 MHz or a Varian CFT 20 instrument for ^{1}H and ^{13}C spectra, respectively.

RESULTS AND CONCLUSIONS

Polymer Structure

NMR spectroscopy was applied to the analysis of the polymer structure for linearity with the results shown in Figure 1, for the 270 MHz ^{1}H spectrum. Both ^{1}H and ^{13}C NMR analyses indicated that all polymers obtained were essentially only para-substituted and free of chain branching.

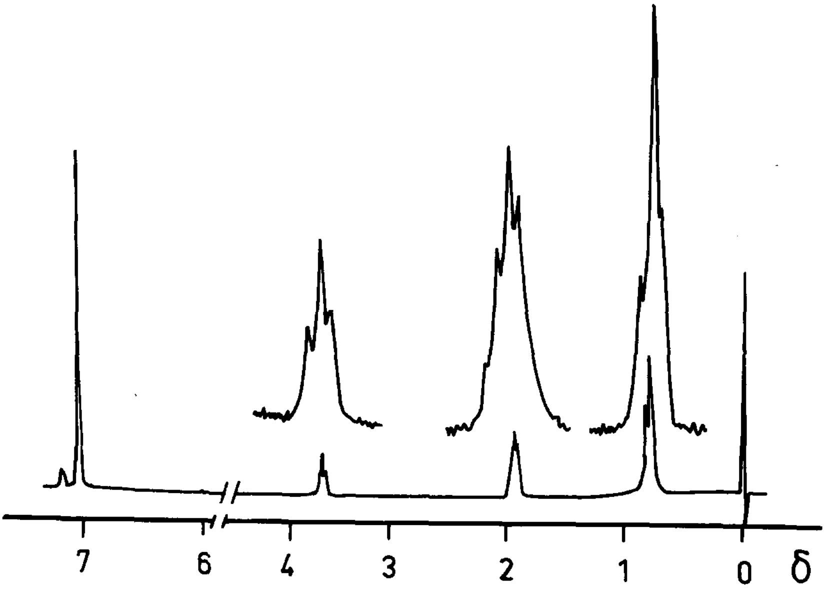


Fig. 1 ^{1}H NMR spectrum of poly-α-ethylbenzyl at 270 MHz

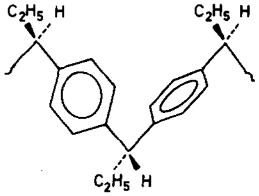
TABLE 1. Chemical shift assignments, δ, in the ^{1}H and ^{13}C NMR spectra of poly-α-ethylbenzyl chloride [a]

Group	^{1}H Spectrum[b] 270 MHz	^{13}C Spectrum 20 MHz
methyl	0.81 (t, 7)	12.87 (c)
methylene	1.97 (g, 7)	28.97 (t)
methine	3.64 (t, 7)	52.63 (d)
aromatic ring phenyl	-	142.79 (s)
phenylene	7.08 (s)	127.85 (m)

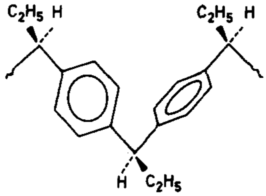
a. The authors are indebted to Prof. A. Watterson of the University of Lowell for providing the ^{1}H spectra. All spectra were obtained on $CDCl_3$ solutions with TMS standard.
b. Peak type and coupling constant are given in brackets.

The chemical shift assignments are collected in Table 1.

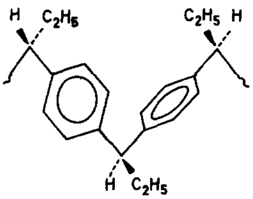
The almost complete absence of extraneous peaks and the lack of peak broadening for any of the protons in Figure 1 indicates that the polymer was also highly stereoregular. It is not possible, however, to conclude whether the stereoregularity is of the isotactic or syndiotactic type, as illustrated below, because both types of triad structures would give simple multiplet structures, although each would be expected to have different chemical shifts as previously observed for poly-α-methylbenzyl[7].



isotactic



syndiotactic



heterotactic

The one indication of irregularities in the polymer structure is the small peak in ^1H spectrum of Figure 1 at 7.21 δ, which is believed to be caused by the minor triad component. From an analogy with the structure of crystalline poly-α-methylbenzyl[4], therefore, it is likely that this polymer is highly isotactic.

Molecular Weight and Distribution

Gelpermeation chromatography was used to evaluate the molecular weight properties of the polymers, particularly the effect of reaction conversion on average and distribution values. The results are collected in Table 2 (relative to polystyrene as a standard)

TABLE 2. Molecular weight properties of poly-α-ethylbenzyl prepared at -100°C[a]

Reaction Time, min.	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
5	5.700	13.000	2.3
15	8.000	18.000	2.3
30	6.700	16.000	2.4
60	7.500	17.000	2.3
120	7.700	17.000	2.2
300	7.500	17.000	2.3
1230	6.300	13.000	2.1
1710	7.000	15.000	2.1

a. Initial reaction mixture contained 8.50 g (55.0 mmol) monomer and 0.50 g (3.7 mmol) $AlCl_3$

for a polymerization reaction in which samples were removed consecutively from a single reaction mixture. The results in Table 2 show that in the polymerization the polymer formed reached a maximum molecular weight in about one hour.Long reaction times resulted in a decrease in molecular weight and a narrowing of the molecular weight distribution towards the most probable values, presumably because of some random degradation process. In comparison, in previous studies on the polymerization of α-methylbenzyl chloride under the same conditions the reaction was completed within five minutes, and no subsequent loss in molecular weight occured[7].

However, the poly-α-ethylbenzyl samples in Table 2 had a monomodal molecular weight distribution while the α-methyl polymer was bimodal. It is possible that as previously suggested the number of peaks in the molecular weight distribution is associated with the number of different types of active species (that is, ions or ion pairs) in the polymerization reaction [8].

Crystalline Properties

Differential scanning calorimetry was applied to determine the melting points and approximate degrees of crystallinity of these polymers. Figure 2 shows a typical thermogram of a polymer as prepared and also after annealing. The melting point of the polymer was approximately 95°C, which is much lower than that of poly-α-methylbenzyl of the same molecular weight, and annealing at 70-80° had little effect on this property .

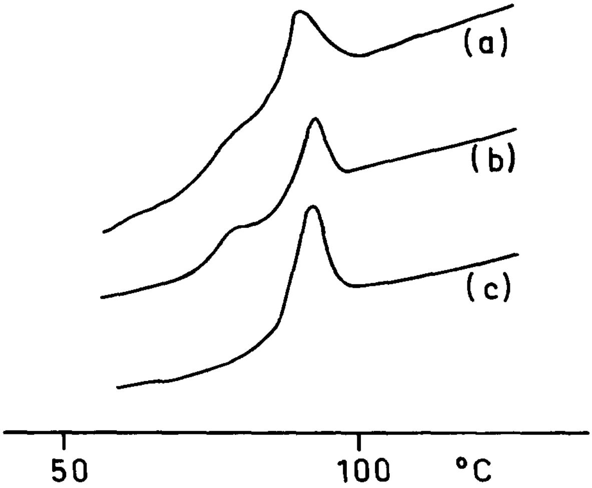


Fig. 2 DSC thermogram of poly-α-ethylbenzyl: (a) as polymerized, (b) after annealing for 24 hours at 70°, and (c) after annealing for 48 hours at 80°

A decrease in melting point with increasing size of the substituents is often observed within a given series of polymers (for example, in polyacrylates or methacrylates) but the extent of the decrease in the present case seems to be unusually large. This relatively large decrease compared to the α-methyl polymer, however, is not believed to be due to any significantly lower stereoregularity in the α-ethyl polymer.

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