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Initiators

Cationic Polymerization of Isobutylene Initiated by Diol/Boron Trichloride Systems

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Abstract:

Cationic polymerizations of isobutylene initiated by 2,5-dimethyl-2,5-hexane diol (HMD) and bis-para-2-hydroxy-2-propylbenzene (BPP) / BCl_3 were carried out in CH_2Cl_2 solution at -30°C,in presence or in absence of 2,6-ditert-butylpyridine (DtBP).IR, ^1H NMR and C^{13} NMR analysis of the resulting polyisobutylenes (PIB) show the insertion of the diol skeleton in the polymers.GPC chromatograms show that the presence of DtPB prevents protonic initiation.The synthesis of PIB with phenolic end groups was carried out by alkylation of α,ω unsaturated oligoisobutylene in CH_2Cl_2 at -30°C initiated by $SnCl_4$.Previously,the alkylation was carried out on a model:2,2,4-trimethyl pentene (TMP).Spectroscopic analyses show that the alkylation takes place mainly on para-position.UV titration of phenyl ring and chemical titration of chlorine show that the functionality of PIB is 2.

Introduction.

Nguyen and Kennedy (1,2,3) have shown recently that tertiary alcohols (both aliphatic and aromatic) in association with BCl_3 are efficient initiating systems for the cationic polymerization of isobutylene.The presence of DtBP greatly diminishes the effect of protonic initiation and has no influence on the relative polymerization.In the present paper we report the synthesis of α,ω dichloro- and of α,ω dihydroxyphenyl-oligoisobutylenes using HMD and BPP/BCl_3 systems as initiators.

Experimental.

Polymerizations were carried out in a glass reactor equipped with a magnetic stirrer.Chemicals were purified,dried,and transferred under vacuum.A mixture of diol (1-1.5 g),isobutylene (27-30 ml),DtBP (1 ml) and CH_2Cl_2 (250 ml) was cooled to -30°C,and neat BCl_3 (3 ml) was introduced.After 45 minutes the reaction was stopped by addition of methanol.CH_2Cl_2 was removed and the residue was dissolved in hexane,washed with water,dried and filtered.After evaporation of hexane,PIB was dried under vacuum.

The synthesis of phenol derivatives were carried out in an all glass reactor flushed with nitrogen.In the case of model study,a solution of TMP ($3\ 10^{-2}$M) and phenol ($3.5\ 10^{-2}$M) in CH_2Cl_2 (100 ml) was cooled to -30°C and $SnCl_4$ ($3\ 10^{-1}$M) was added.After 1 hour,the reaction was stopped by introduction of methanol.After several times washing with water,CH_2Cl_2 was removed and the residual mixture was distilled under vacuum.In the case of PIB,dehydrochlorination was carried out by heating (100°C) under vacuum for 2 hours. The resulting α,ω divinylpolyisobutylene was alkylated in the same way as TMP.IR (Perkin -Elmer 577), ^1H NMR (Varian EM 390,CCl_4 solvent,TMS reference), ^{13}C NMR (Brucker WP 80,$CDCl_3$ solvent,TMS reference),and UV (Perkins-Elmer 219,hexane solvent) were used to analyze end-groups.Molecular weights of PIB were determined by GPC (Waters,10^4A,10^3A,500A,500A,columns μstyragel,THF as solvent).

Results and Discussions.

a/ Polymerizations of isobutylene initiated by Diol/BCl_3 systems.

The results are reported in table I.

Table I

Isobutylene polymerizations initiated by diol/BCl_3 systems, in absence or in presence of DtBP. Solvent CH_2Cl_2, T=−30°C, polymerization time: 45 min.

Exp	[Diol] 10^2 M		[IB] M	[DtBP] 10 M	[BCl_3] 10 M	Yield %	GPC		
							$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
1	HMD*	4.6	1.6	0	2	100	2770	1730	1.6
2	HMD	4.1	1.6	1.8	1.4	25	1650	1230	1.3
3	BPP	2.2	1.2	0	2	90	7480	4250	1.7
4	BPP	2.0	1.1	1.8	1.4	75	3220	2750	1.2

* polymerization time: 2 hours

GPC chromatograms are reported in Figure 1. In absence of DtBP (a) the curve is bimodal and can be decomposed by deconvolution: Part I: $\overline{M}_w$=5220, $\overline{M}_n$=4380 (32%), Part II: $\overline{M}_w$=1550, $\overline{M}_n$=1280 (68%).

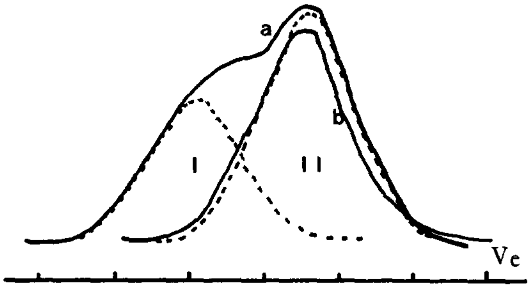

Figure 1 : GPC traces of PIB initiated by HMD/BCl_3 system. a/in absence of DtBP, b/in presence of DtBP.

Using the initiating system bis-para-2-chloro-2-propenylbenzene/BCl_3, Nuykens and al. (4,5) obtained the same type of chromatograms. The high molecular weight was attributed to the protonic initiation, and the low value to the initiating system used. In presence of DtBP (b) the chromatogram is monomodal. This fits Nuykens 's results.

Another explanation is to suppose that the mixture of diol and BCl_3 may proceed by two different paths:

$$\text{HO-R-OH} + BCl_3 \begin{array}{l} \nearrow \; HOR^{\oplus}\,,\; BCl_3OH^{\ominus} \qquad 1 \\ \searrow \; H^{\oplus}\,,\; BCl_3OROH^{\ominus} \qquad 2 \end{array}$$

Each of these separately initiates the polymerization and,the termination reactions being different,the resulting polymers have different molecular weights.However,a study of the interaction between alcohol and BCl_3 (1) in absence of monomer showed that ionization reaction proceeds only via path 1. Thus,initiation by protons is due to the moisture remaining in the system but the presence of DtBP by trapping the protons prevents this initiation.

b/ Syntheses of phenol derivatives.

The synthese of phenol derivatives has been first reported by Russell and al. (6).Recently,Kennedy and al. (7) have used an alkylation reaction of phenol initiated by a Lewis acid in hot hexane.We chose to use the alkylation of phenol initiated by $SnCl_4$ in CH_2Cl_2 at -30°C (see experimental).The reactions with the TMP isomers gave a mixture of two products which were separated in a liquid (L,60%) and in a solid (S,40%) phase . ^{1}H NMR analysis showed that,according to Francis and Archer (8),L,is a mixture of tetraisobutylene isomers (TTI).The IR spectrum of S presents a peak at 3590 and a doublet at 1605-1595 cm^{-1}.Comparison with phenol spectrum showed that it is an alkylated phenol.

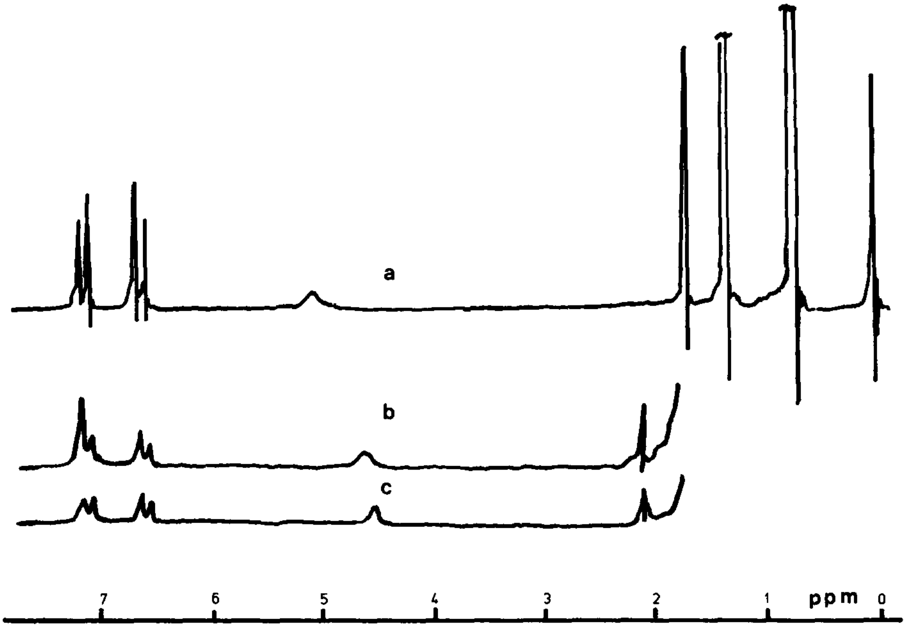

Figure 2 : ^{1}H NMR spectra of phenol derivatives.a/TMP phenol,b/PIB initiated by BPP/BCl_3,c/PIB initiated by HMP/BCl_3.

Figure 2a indicates that the alkylation occurs on para-position (AB system,2 doublets centered at 6.85 ppm). ^{13}C NMR (Figure 3a) gives other evidence of this para-alkylation.

From the above results,the reactions of TMP isomers-$SnCl_4$-phenol systems may be interpreted by the following scheme:

$$\begin{array}{lllll}
\text{ionization} & H_2O + SnCl_4 & \longrightarrow & H^{\oplus},SnCl_4OH^{\ominus} & \\
 & TMP + H^{\oplus} & \longrightarrow & TMP^{\oplus} & \\
\text{dimerization} & TMP^{\oplus} + TMP & \longrightarrow & TTI^{\oplus} \longrightarrow & TTI + H^{\oplus} \\
\text{or alkylation} & TMP^{\oplus} + \phi\text{-}OH & \longrightarrow & TMP\text{-}\phi\text{-}OH + H^{\oplus} &
\end{array}$$

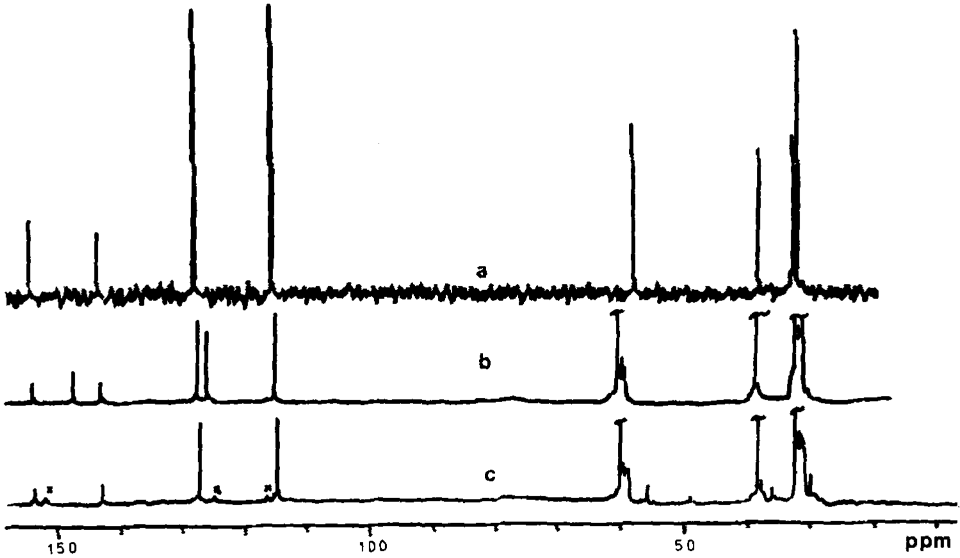

Figure 3 : ^{13}C NMR spectra of phenol derivatives.a/TMP phenol,b/PIB initiated by BPP/BCl$_3$,c/PIB initiated by HMD/BCl$_3$.

* peaks of ortho-alkylation

Thus,it appears that alkylation competes with dimerization reaction.However,it is worth mentioning that alkylation occurs with both internal and external double bonds.In the case of PIB resulting from HMD and BPP/BCl$_3$ initiating systems,the thermal dehydrochlorination gives 30% of internal and 70% of external olefins (^{1}H NMR spectrum :peaks at 5.1,4.9,4.7 ppm,IR spectrum : peak at 1640 cm^{-1}).After alkylation,the IR spectrum no longer shows the peak at 1640 cm^{-1} but new peaks are present at 3550,1610,1595 cm^{-1}. ^{1}H NMR spectra (Figure2b and 2c) exhibit two doublets centered at 6.8 ppm;the peak at 7.18 ppm (Figure 2b) corresponds to the benzene ring of BPP in the polymer chain.Moreover,the peaks at 5.1,4.9,4.7 ppm have completely disappeared.As in the case of TMP,these results indicate that alkylation takes place on para-position; ^{13}C NMR (Figure 3b and 3c) also confirms this tendency and only a small amount of alkylation on ortho-position was detected.

c/ UV titration of benzene ring.

The functionality of PIB can be determined by UV titration of the benzene ring.In the following:f=number of benzene ringsper chain,m=weight (g) of PIB in a solution of volume V,M=molecular weight of PIB,C_ϕ=concentration in benzene rings of the solution,n_ϕ=number of benzene rings in m g of PIB,D=optical density of the PIB solution;$n_\phi=fm/M$ and $C_\phi=n_\phi/V=fmMV=D/\varepsilon l$,then $f=DMV/\varepsilon lm$

This titration is possible only if the value of ε of PIB phenol is known. We considered that p-tert-amylphenol (PTAP) is a good model of PIB phenol and we assumed that both compounds have the same ε.

Figure 4 : UV spectra of : a/ PTAP, b/ TMP phenol

The UV spectrum of PTAP in hexane exhibits a spread absorption in the range 290-260 nm (corresponding to a forbidden transition) and a peak at 195 nm with a shoulder at 222 nm. In principle, titration is possible only for non overlapping peaks. For this reason, we carried out two independent titrations: one using the area of the spread absorption (290-260 nm) and the other using the peak at 195 nm, neglecting the overlapping of the shoulder at 222 nm.

The spectra of TMP phenol and PIB phenol have the same shape as that of PTAP (only a small shift of 1 nm). The corresponding ε have been determined: $\varepsilon_{195} = 44,000$ and $\varepsilon_s = 640$.

Table II shows the results obtained from absorptions at 195 and 290-260 nm. The experimental value of f is close to the theory. Thus, we can reasonably assert that the functionality of PIB initiated by diol/BCl_3 is two.

An additional proof is given by the chemical titration of chlorine: for PIB resulting from the initiation by BPP/BCl_3, the experimental percentage is is 2.1 instead of 2.2 for the theory.

Table II

UV titration of benzene rings of PIB phenols in hexane solution using peak at 195 nm and spread absorption at 290-260 nm.

PIB phenol	m 10^2.g	V 10^2.l	D 195	S 290-260	$\bar{M}$	l cm	f Exp.	f Th.
HMD	1.94	2	-	0.76	1650	1	2.02	2
	1.94	2	0.5	-	1650	0.01	1.93	2
BPP	2.2	2	-	0.70	3220	1	3.20	3
	2.2	2	0.5	-	3220	0.01	3.32	3

In conclusion,we showed that the tertiary diols (both aromatic and aliphatic) in combination with BCl_3 are efficient initiating systems for the cationic polymerization of isobutylene;the resulting oligomers are bifunctional.We have also proved that the alkylation at low temperature is quantitative and nearly always on the para-position.

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