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Effect of the Initiator Anion and of the Polarity of the Medium on the Intra-Intermolecular Growth in the Cationic Polymerization of 2,5-Dimethyl-1,5-hexadiene*

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SUMMARY

The influence of solvents and catalysts on the formation of soluble and insoluble polymer during cationic polymerization of 2,5-dimethyl-1,5-hexadiene was studied. In nonpolar medium (n-heptane or without solvent) the amount of the insoluble part is dependent on the catalyst used and increases as follows: $BF_3 \ll AlBr_3 < TiCl_4$. Especially soluble polymers are obtained in a solution of methylene chloride or in a mixture of methylene chloride-nitrobenzene. The temperature range studied, -30° to -78°, did not show any important influence on the polymer composition. It was found that the bulky anion of the initiator and the polarity of the medium considerably influenced cyclization during intra-intermolecular propagation of the polymer chain.

INTRODUCTION

The effect of the counterion from a catalyst on the structure of a growing polymeric chain has been observed in the steroregular polymerization of vinyl

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monomers catalyzed with soluble ionic catalysts. In the cationic polymerization of tert-butyl vinyl ether catalyzed with boron trifluoride etherate, it has been ascertained experimentally that a polymer having the isotactic structure is mainly formed in nonpolar solvent polymerization, whereas polymerization in a sufficiently polar medium leads prevailingly to the syndiotactic structure [1, 2]. The same results have been obtained for the anionic polymerization of methyl methacrylate with soluble organometallic compounds [3]. The formation of the isotactic structure in a nonpolar solvent is ascribed to the influence of the catalyst counterion on the growth reaction; this counterion forms an ionic pair with the growing polymeric chain (undissociated from the growing end). In polar solvents, where the ionic pairs are more solvated and are near to the free ionic state, the propagation reaction is influenced by the counterion very slightly, and a polymer with syndiotactic structure is obtained.

It is known that in the polymerizations of nonconjugated dienes [4] and α-diolefins [5], proceeding by the intra-intermolecular mechanism, the monomeric units are incorporated into the polymeric chain by both their double bonds, which is followed by the formation of cyclic units repeatedly occurring in the chain. The polymers thus formed are therefore soluble and have only a low content of double bonds. Not all the monomeric units, however, participate in the growth reaction by both bonds; some of them are incorporated by one bond only. The noncyclized units can use the remaining double bond for participating in a further reaction leading to the formation of branched or cross-linked polymers. This is why in the polymerization of 1,5-hexadiene [5, 6], apart from the soluble polymer, a great amount of the insoluble one is also formed. We found in our previous work [7] that the amount of insoluble polymer formed by the solution cationic polymerization of 2,5-dimethyl-1,5-hexadiene depended on the catalyst used and on the polarity of the solvent.

In this work, the effect of the reaction conditions on the structures of the polymers of 2,5-dimethyl-1,5-hexadiene prepared by the cationic polymerization with various Friedel-Crafts catalysts in solvents of various polarities has been investigated.

EXPERIMENTAL

The polymerizations were carried out under dry argon in a glass reaction vessel provided with a magnetic stirrer, a three-way stopcock, and a sodium hydride seal. The last traces of moisture were removed by heating the reactor over a direct flame, followed by flushing during a 30-min period with a mild stream of argon which had been dried over sodium hydride. The following components were gradually introduced into the reactor: solvent and monomer (in a stream of dry argon), and cocatalyst and catalyst (upon thermostating to the temperature required). As catalysts, boron fluoride was used in the gaseous state, aluminium bromide and trichloroacetic acid were dissolved in n-heptane, and titanium(IV) chloride was used without any solvent. To remove the occluded moisture, the syringes were washed several times immediately before use with n-heptane which had been dried over sodium hydride. The total volume of the reaction mixture in the vessel was 7 ml. When the reaction had stopped following the addition of 0.5 ml of ether, the content of the reaction vessel was poured out into 20 ml of n-heptane. The mixture was then shaken three times with water acidified with hydrochloric acid, and the polymer was filtered from the insoluble hydrocarbon layer, washed with n-heptane, dried at 50°C/20 Torr, and weighed. The soluble polymer was precipitated by acetone from the filtrate upon concentrating to a 10 to 20 ml volume, separated, and weighed after removal of volatile fractions.

The preparation, purification, and drying of the monomer [8], boron trifluoride [9], titanium(IV) chloride [7], and n-heptane [10] were described earlier [7]. The trichloroacetic acid was purified by distillation and dried with phosphorus pentoxide in a solution of n-heptane. Aluminium bromide [11] was prepared by a direct reaction of metallic aluminum shavings with bromide and purified by distillation.

Crystallographic structures of the soluble samples of poly-2,5-dimethyl-1,5-hexadiene were determined from diffraction diagrams obtained with a Hilger & Watts powder diffractometer, using the CuKa radiation. Molecular weights of the polymer samples were determined by the cryoscopic method in cyclohexane of spectral purity.

RESULTS

The polymerizations of 2,5-dimethyl-1,5-hexadiene at -78°C were carried out without solvent, in 50 or 80 vol-% n-heptane, methylene chloride, and in a methylene chloride-nitrobenzene mixture (1:1 vol). As catalysts, BF_3 (100 to 200 cm^3 gas per 7 ml of reaction mixture), $AlBr_3$ (0.04 to 0.055 mole/l), or $TiCl_4$ (0.1 to 0.4 mole/l) were used, with trichloroacetic acid as cocatalyst.

Cocatalysis with Trichloroacetic Acid. The polymerization catalyzed with $TiCl_4$ in the absence of cocatalyst did not occur, under the given experimental conditions, until trichloroacetic acid was added. The cocatalytic effect of trichloroacetic acid could be observed as a steep increase in the reaction temperature after the acid had been added to the reaction mixture. This was also true in the polymerization catalyzed with $AlBr_3$.

The Effect of the Kind of Catalyst and of Conversion on the Composition of Polymer. In the polymerizations without solvent and in n-heptane solution, the insoluble polymer has always separated from the reaction mixture as a swollen gel in an amount depending on the catalyst used, the catalyst series being $BF_3 \ll AlBr_3 < TiCl_4$ (Table 1 and 2); the amount of the insoluble polymer increased with conversion (in Table 2 see catalysis with $TiCl_4$).

Table 1. Polymerization of 2,5-Dimethyl-1,5-hexadiene at -78°C in the Absence of Auxiliary Solvent

Catalyst-cocatalyst	Conversion (wt %)	Polymer fractions (wt %)	
		Soluble	Insoluble
BF_3, (H_2O?)	76.5	94.2[a]	5.2
BF_3-CCl_3COOH	83.5	100	–
$AlBr_3$, (H_2O?)	73.0	26.5	73.5
$AlBr_3-CCl_3COOH$	68.5	55.7	44.3
$TiCl_4-CCl_3COOH$	89.0	25.5[b]	74.5

[a] $\bar{M}_n = 1700$.
[b] $\bar{M}_n = 760$.

Effect of the Type of Solvent and Temperature on the Composition of Polymer. The effect of solvents of various polarity on the formation of insoluble polymer in the polymerization catalyzed with $TiCl_4$ is shown in Table 3. In 50% n-heptane solution, insoluble polymer is mainly formed, whereas in methylene chloride at the same concentration only soluble polymer is obtained. If, however, the concentration of the monomer in methylene chloride is increased to 80%, the polarity of the medium decreases to such a value that the insoluble polymer already appears in a considerable amount. If the mixed solvent methylene chloride-nitrobenzene is

Table 2. Polymerization of 2,5-Dimethyl-1,5-hexadiene at -78°C in n-Heptane Solution

Catalyst-cocatalyst	[M] (vol %)	Conversion (wt %)	Polymer fractions (wt %)	
			Soluble	Insoluble
$BF_3, (H_2O?)$	50	81.6	95.5	4.5
	80	98.1	92.9	7.1
BF_3-CCl_3COOH	50	84.9	100.0	–
	80	93.5	100.0	–
$AlBr_3, (H_2O?)$	80	85.1	17.7	82.3
$TiCl_4-CCl_3COOH$	50	22.6	94.3	5.7
		75.0	73.5	26.5
		94.0	15.5	84.5
	80	95.0	4.8	95.2

Table 3. Effect of the Polarity of the Medium on the Polymer Composition in the Polymerization at -78°C with a $TiCl_4-Cl_3CCOOH$ Catalytic System

Solvent	[M] (vol %)	Conversion (wt %)	Polymer fractions (wt %)	
			Soluble	Insoluble
C_7H_{16}	30	89.0	18.1	81.9
	50[a]	94.0	15.5	84.5
	80	95.0	4.8	95.2
CH_2Cl_2	30	85.0	100.0	–
	50	78.0	100.0	–
	80	99.0	24.4	75.6
$CH_2Cl_2-C_6H_5NO_2$[b]	80	84.5	100.0	–

[a] At -50 and -30°C, conversions are 87.6 and 79.1%, respectively; the amounts of soluble polymer are 24.8 and 21.2%, and of insoluble polymer 75.2 and 78.8%, respectively.

[b] Volume ratio 1:1.

used in the polymerization, the entire polymer formed is soluble, even at a monomer concentration of 80%, due to a further increase in the polarity of the solvent. In the 30 to 78°C temperature range, the polymerization temperature does not have any considerable effect on the composition of the polymer formed in the nonpolar medium.

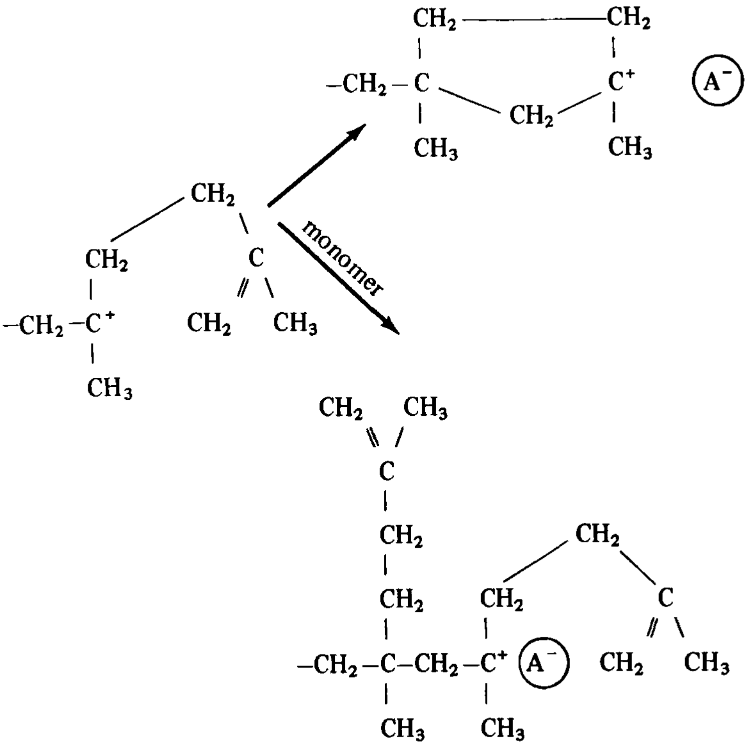
Characteristics of the Polymers. The diffraction diagrams of the soluble samples of poly-2,5-dimethyl-1,5-hexadiene have a wide reflection with a maximum at $2\theta = 14°$. It follows from the nature of the diffraction diagram that the polymers have an amorphous structure, independent of the conditions of preparation and of the catalysts used.

The polymers formed in a polar medium or in a medium of higher polarity as dissolved fractions are also soluble in some other solvents, such as ether, benzene, and toluene. The polymers insoluble in the reaction medium could not be dissolved, even if boiling solvents were used. They did not melt on heating to 310°C, and they decomposed at a higher temperature.

DISCUSSION

The effect of the counterion on the growth of nonconjugated dienes which occurs as an intra-intermolecular cyclopolymerization has not been studied. The initiation of the polymerization of 2,5-dimethyl-1,5-hexadiene with the Friedel-Crafts catalysts, investigated under the above experimental conditions, occurs according to the usual proton mechanism. This is corroborated by the necessity of the presence of a cocatalyst, which was shown experimentally. Judging from the effect of the conditions on the formation of the soluble and insoluble polymer, we assume that the type of catalyst used and the polarity of the medium affect the rate of formation of a five-membered ring in the intra-intermolecular propagation of the polymeric chain as shown in the equations. The steric effect of the anion from the catalyst and the dissociation of the ionic pair of the growing end of the polymeric chain control the formation of a soluble (reaction A) or an insoluble (reaction B) polymer.

In the polymerization catalyzed with BF_3 in a nonpolar solvent, the steric effect of the catalyst anion on cyclization is comparatively small; therefore, the rate of intramolecular cyclization prevails over that of intermolecular addition of another monomer molecule, and a soluble polymer having a low content of double bonds is mainly formed. On the contrary,



(A)

(B)

(A^-): $[BF_3OH]^-$, $[TiCl_4\ CCl_3COO]^-$

in the polymerizations catalyzed with $AlBr_3$ or $TiCl_4$ the counterion from the catalyst is much bulkier, thus presenting a much greater steric hindrance to the formation of a five-membered ring. This leads to the prevailing formation of insoluble cross-linked polymers, which—as far as they are still soluble—show a higher degree of unsaturation than polymers of the same molecular weight, prepared with BF_3 as catalyst [7].

In the polymerization in polar solvents it can be assumed that solvatation increases the dissociation of the ionic pair at the end of the growing chain, thus decreasing the effect of the counterion from the catalyst on the growth reaction and enabling the intramolecular cyclization to be the preferred reaction. Therefore, by merely changing the polarity of the solvent, we can, under otherwise identical conditions, prepare polymers ranging from insoluble to the completely soluble ones.

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