

Cationic monomer-isomerization oligomerization of 2-methyl-2-butene

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The polymerizations of 2-methyl-2-butene (2M2B) were carried out by various cationic initiators in different media at 30°C. All these polymerizations generate oily oligomers of rather low degrees of polymerization (3–5). Evidences from i.r. and ¹H n.m.r. show that the oligomer chain contains structural units derived from both 2M2B and 2-methyl-1-butene (2M1B), which indicates that 2M2B isomerizes partially to 2M1B during the polymerization. The unsaturated endgroups also arise from chain transfers of both 2M2B and 2M1B growing carbocations by proton-elimination. The reaction carried out in toluene fails to produce any polymer or oligomer but generates an adduct of 2M2B and toluene by Friedel–Crafts alkylation. Copyright © 1996 Elsevier Science Ltd.

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Introduction

It is well known that the cationic polymerization of 1,2-disubstituted olefins is difficult due to steric hindrance^{1,2}. Isobutylene is a well-demonstrated cationically polymerizable monomer and its polymerization resulting in high molecular weight polyisobutylene is of industrial importance. On the other hand, 2-methyl-2-butene (2M2B), a 1,2-disubstituted olefin which can be regarded as a methyl derivative of isobutylene, has a much lower cationic polymerizability. We became recently interested in the behaviour of the cationic polymerization of this monomer because of its importance in the synthesis of piperylene-2M2B copolymer-based aliphatic petroleum resins³. The publications about the cationic polymerization of 2M2B are quite limited. Lohuizen *et al.*⁴ carried out the cationic polymerization of 2M1B by AlCl₃ and AlBr₃ at –175°C with a small amount of 2M2B and found that 2M2B has a strong reduction effect on the yield and molecular weight of the polymer. Imanishi *et al.*⁵ polymerized 2M2B by TiCl₄ at –78°C and obtained an oligomer with a low degree of polymerization. These authors did not show any data about the 2M2B oligomer microstructures.

The present work describes the cationic monomer-isomerization oligomerization of 2M2B which has never been reported in existing literature. In this work we perform the polymerization of 2M2B by various cationic initiators at a much higher temperature (30°C). The polymerization under this condition produces oligomers of rather low degree of polymerization, which enable us to determine with ease structures of unsaturated endgroups so as to obtain more insight into oligomer microstructure, chain transfer and monomer-isomerization during the polymerization.

Experimental

Materials. 2M2B from Fluka was distilled over CaH₂. Solvents were also purified by distillation over CaH₂. AlCl₃ was purified by sublimation in vacuum. BF₃OEt₂, TiCl₄ and triflic acid (HOTf) were used as received.

Polymerization. The polymerization was carried out in a three-necked-reactor in nitrogen atmosphere. The solvent and initiator were introduced first and 2M2B was added by syringe. After 1.5 h the polymerization was quenched with the methanol-containing solvent. The resulting solution was washed by water. The oligomer was recovered by evaporation of the solvent and unreacted monomer.

Measurements. I.r. of the oligomers was measured by a NICOLET MX-1 spectrometer and ¹H n.m.r. spectra were recorded by a VARIAN FT-80A spectrometer.

Results and discussion

Table 1 shows the results of polymerizations of 2M2B by various cationic initiators in different solvents. All these polymerizations produce oily oligomers in partial yields. Although the propagating carbocation has a similar structure to that resulting from isobutylene, chain growth hardly takes place due to the steric hindrance exerted by β-methyl groups of 2M2B.

Figures 1 and 2 show i.r. and ¹H n.m.r. spectra of the oligomers. The signals of unsaturated protons can be clearly observed on these spectra, which indicates that the chain transfer of growing species to monomer through proton-elimination actively presents during the polymerization. By assuming that the growing chain is stopped only by this process⁶ we can calculate the degree of polymerization (*DP*) with the integration intensities of unsaturated and saturated protons on the ¹H n.m.r. spectra shown in Figure 2. As indicated in Table 1, all the polymerizations produce oligomers with quite limited *DP* values.

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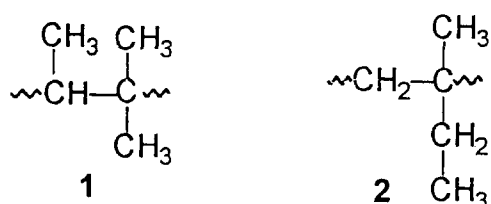
Table 1 Polymerizations of 2M2B by various cationic initiators in different solvents^a

Run no.	Initiator	Solvent	Yield (%)	DP ^b	Endgroup fraction (%) ^b	
					II + III	IV + V
1	HOTf	<i>n</i> -Heptane	78	3	10	90
2	BF ₃ OEt ₂	<i>n</i> -Heptane	75	3	15	85
3	TiCl ₄	<i>n</i> -Heptane	23	4.5	20	80
4	AlCl ₃	<i>n</i> -Heptane	90	5	5	95
5	AlCl ₃	CH ₂ Cl ₂	29	4	12	88
6	AlCl ₃	Toluene	~100		Adduct of 2M2B and toluene	

^a[2M1B] = 2.0 mol l⁻¹; [Initiator] = 0.02 mol l⁻¹; reaction temperature: 30 °C; time: 1.5 h

^bCalculated from the integral intensities of unsaturated protons on ¹H n.m.r.

It is interesting to note on the i.r. spectra (Figure 1) that two types of unsaturated endgroups, disubstituted and trisubstituted double bonds (>C=CH₂ and >C=CH-), present in the oligomers. As the latter can only be generated by chain transfer of growing species resulting from 2M1B but not from growing species derived from 2M2B, we conclude that two monomers,



2M2B and 2M1B, are involved in the propagation process and the resulting oligomer chain contains both 2M2B units (1) and 2M1B units (2).

¹H n.m.r. spectra of the oligomers shown in Figure 2 give us a clearer evidence for the presence of both structural units 1 and 2. We observe in the region of saturated protons a signal at 1.25 ppm (peak b) which is attributed to saturated protons of -CH₂- groups. Obviously, this kind of group is contained only in structural unit 2 generated from 2M1B but not in unit 1 produced by 2M2B.

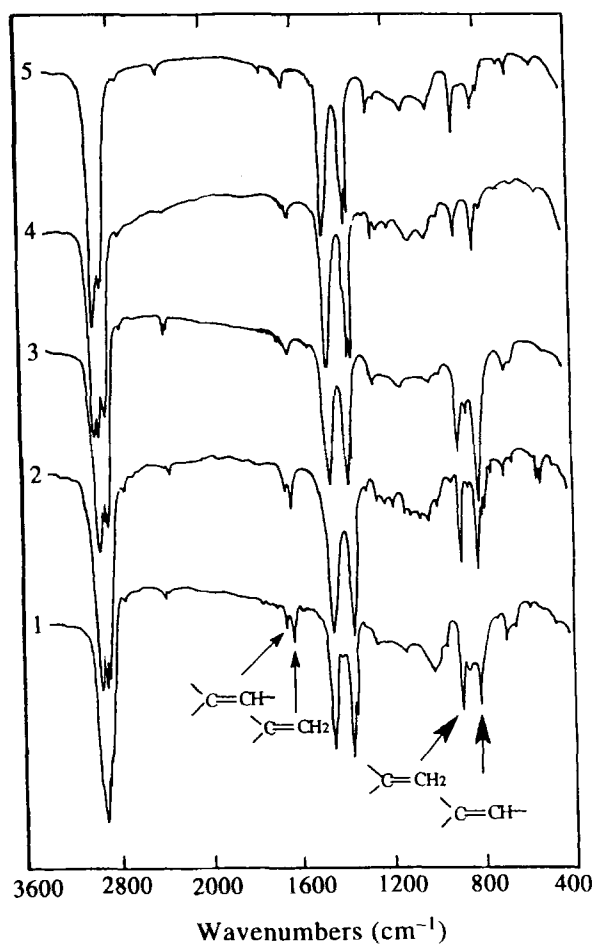


Figure 1 I.r. spectra of 2M2B oligomers. Reaction conditions in Table 1. 1, Run 1; 2, Run 2; 3, Run 3; 4, Run 4; 5, Run 5

Structural units	Chain endgroups		
1 	I 	II 	
2 	III 	IV 	V

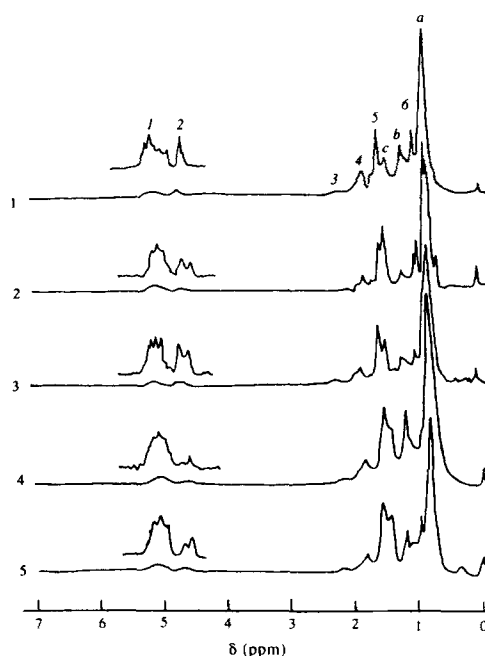
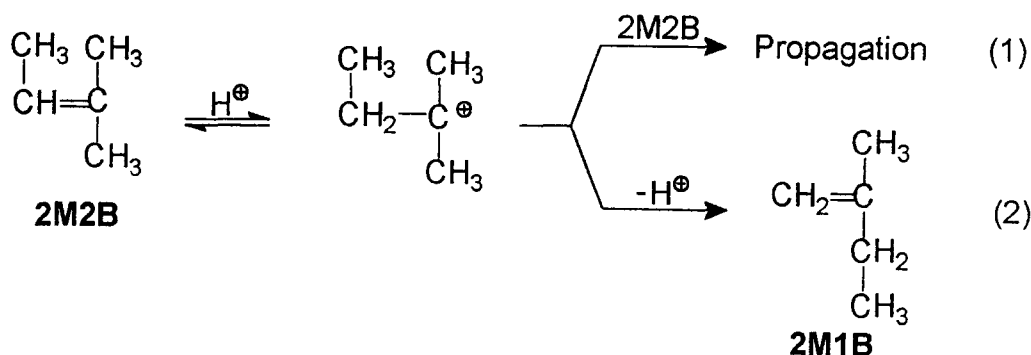


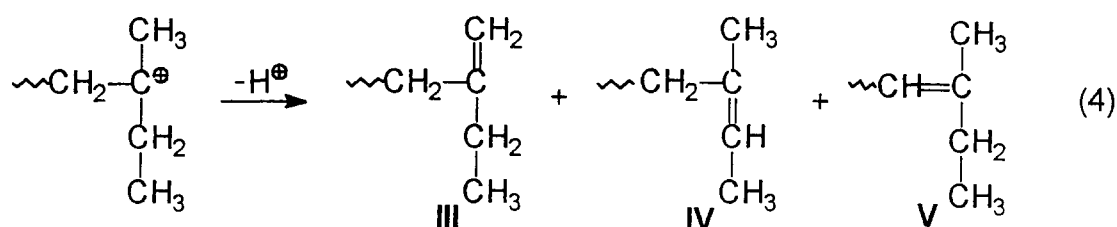
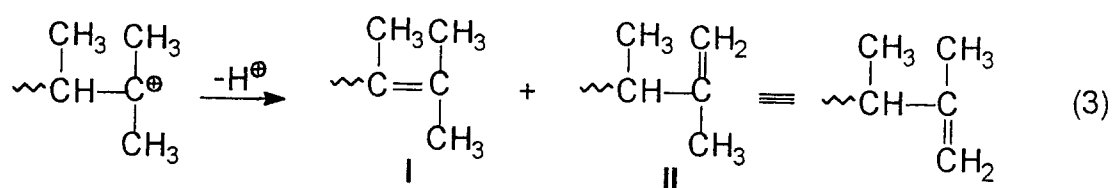
Figure 2 ¹H n.m.r. spectra of 2M2B oligomers. Reaction conditions in Table 1. 1, Run 1; 2, Run 2; 3, Run 3; 4, Run 4; 5, Run 5

To explain the result that both 2M2B and 2M1B are incorporated in the oligomer chains, we propose that a monomer-isomerization takes place through a consecutive protonation-deprotonation process as follows:



According to the above scheme, the protonated 2M2B can pursue a propagation (1) as well as a deprotonation (2) to isomerize to 2M1B which enters oligomer chains later. The propagation reaction seems strongly inhibited by the steric hindrance of β -methyl of the monomer, while the deprotonation is quite likely to occur, as observed by Higashimura⁷ in the cationic monomer-isomerization of 2-ethyl-1,3-butadiene.

Based on the above monomer-isomerization proposition, we can visualize two chain transfer reactions corresponding to the two growing carbocations derived from 2M2B and 2M1B, respectively:



The chain transfer (3) produces unsaturated endgroups I giving no ¹H n.m.r. signal and II ($>\text{C}=\text{CH}_2$) which gives signal 2 at 4.67 ppm. The chain transfer (4) generates endgroups III, IV and V. III contributes also to peak 2 while both IV and V possess structure $>\text{C}=\text{CH}-$ and give signal 1 at 5.15 ppm. Therefore, with the integration

intensities of signals 1 and 2 we have been able to calculate the proportions of the unsaturated endgroups II, III, IV and V, which are summarized in Table 1. It is worthy to note that endgroups IV and V generated from

2M1B represent a large proportion, which indicates that the isomerization process from 2M2B to 2M1B is prevalent in this reaction system under our experimental conditions.

The prevalence of the monomer-isomerization reaction reveals that the carbocation is reluctant to propagate with 2M2B as shown in reaction (1) due to the steric hindrance of the monomer, but is likely to pursue other reaction routes. This consideration can be further rationalized by results of the reaction of 2M2B in toluene. In fact, the cationic polymerization of 2M2B in toluene, a frequently used solvent for cationic polymer-

izations, fails to produce any oligomer or polymer but generates an adduct of 2M2B and toluene, as shown in Figure 3. It is well known that the carbocation is ready to undergo a transfer to aromatic compounds by Friedel-Craft alkylation. We conclude therefore that the protonated 2M2B undergoes directly a complete alkylation

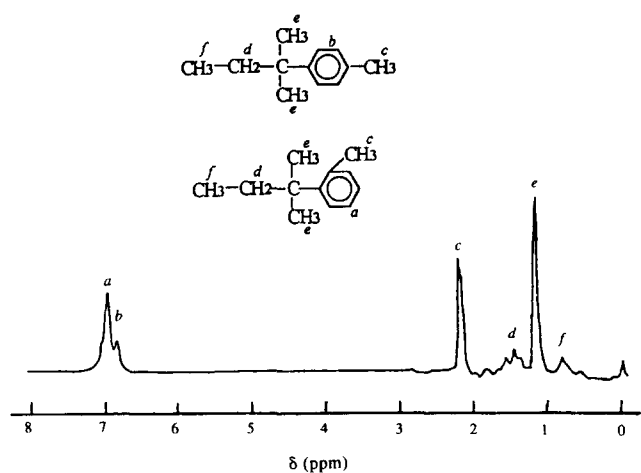
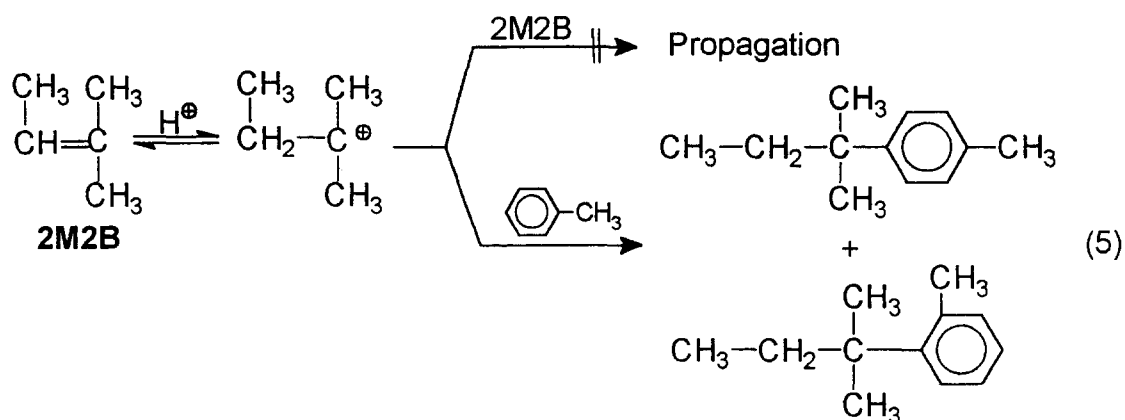


Figure 3 ^1H n.m.r. spectrum of the adduct of 2M1B and toluene (Run 6 in Table 1)

reaction with toluene but does not pursue a strongly hindered propagation. This process can be illustrated schematically in reaction (5):



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