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Polymerization of Methane and Olefin Mixtures over Fluosulfonic Acid and Antimony Pentafluoride

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ABSTRACT

Mixtures of methane and olefins (ethylene, propylene, butenes, butadiene, and styrene) have been polymerized over $\text{HSO}_3\text{F-SbF}_5$ to yield an oily oligomer with a molecular weight ranging from 100 to 700. The NMR spectra of each polymer showed a sharp peak at or near 1.25δ , suggesting the presence of block methylene in the polymer. The formation of block methylene is surprising considering the fact that the polymerization reaction is carbonium ion in nature. A primary cation has been invoked to explain the results. The formation of this primary cation must involve some extraordinary stabilization by some component in the acid.

In the previous paper [1] it was revealed that alkanes can be polymerized (polycondensed) in $\text{HSO}_3\text{F-SbF}_5$ to polymeric materials. It was also reported that methane gave a very low yield of polymer. In an attempt to improve this yield, small amounts of various olefins

were included as reactants with the methane. The reaction procedure consisted of adding a gaseous mixture of methane and approximately 1 to 2% by weight of an olefin to an autoclave containing a 1:1 ratio of $\text{HSO}_3\text{F-SbF}_5$ at room temperature. The gaseous feed mixture was added at various times during the reaction and the total reaction was run for 24 hr. Approximately 4 moles of hydrocarbon were added per mole of acid. After completion of the reaction the polymer was recovered by quenching at -78°C with $\text{NaOCH}_3/\text{CH}_3\text{OH}$. The yield (weight of polymer obtained divided by the total weight of hydrocarbons added to the reactor) of the polymer was greatly increased by this addition of olefin as shown in Table 1. Analysis indicated at least one-half of the olefin was polymerized while the rest was reduced to the corresponding alkane or cleaved. The polymeric products were tan-to-red, oily polyalkanes with a molecular weight as determined by mass spectra ranging from 100 to 700. The mass spectra showed peaks at every mass unit from 100 to 700 inclusive. The largest peaks were 13 to 15 mass units apart. Elemental analysis of a polymer derived from methane and propylene was 77.5% C, 10.0% H, and 4.6% S; the remainder was probably oxygen present as oxides of sulfur. Only trace amounts of fluorine and antimony were present in the polymer. The NMR spectra of each of the polymers in CCl_4 showed a sharp peak at or near 1.25δ , suggesting the presence of block methylene (at least four adjacent CH_2 units) in the polymer since polyethylene and block copolymers of ethylene give strong singlets around 1.25δ .

TABLE 1. Copolymerization of Methane and Olefins

Olefin used	Wt% conversion of reactants to polymer ^a	% Block $-\text{CH}_2-$ in polymer
None	0.2	50
Ethylene	5	20
Propylene	10	25
Butene-1	2.5	20
Isobutylene	5	20
trans-Butene-2	2	5
Butadiene	6	20
Styrene	-	35

^aReactions run at room temperature for 24 hours at a 1:1:4 $\text{HSO}_3\text{F-SbF}_5$ -hydrocarbon molar ratio.

(Polyethylene in carbon tetrachloride at 50°C gives one peak in the NMR at 1.20 δ .) The NMR spectrum of polypropylene made over $\text{HSO}_3\text{F-SbF}_5$ showed no such peak at 1.25 δ .

The NMR spectra of polymethane and a polymer synthesized from methane and propylene are shown in Figs. 1 and 2, respectively. The peak due to the block methylene is indeed surprising considering the fact that the polymerization reaction is carbonium ion in nature. The expected products from a cationic-type mechanism should be highly branched as reported earlier [1]. Integration of the spectra for each polymer in Table 1 showed that each of the products contained 5 to 50% block methylene. Further evidence for the polymerization of methane is revealed by the NMR of the polymer obtained from the reaction of methane and styrene (δ , CDCl_3): 0.8 (CH_3 , 3), 1.3 (CH_2 , 4.5), 2.2 (CH_2 , 2), 2.6 (ArCH and/or $\text{C}=\text{CCH}$, 1) and 7.3 (C_6H_5 , 1.5). The aromatic to aliphatic hydrogen ratio was 1:6, indicating at least 10 molecules of methane have been polymerized per molecule of styrene since the ratio would be 5:3 if the polymer were pure polystyrene. It is not known whether the polymers obtained are mixtures of homopolymers of methane initiated with an olefin and the polyolefin or a copolymer of methane and olefin or a combination of both. The results

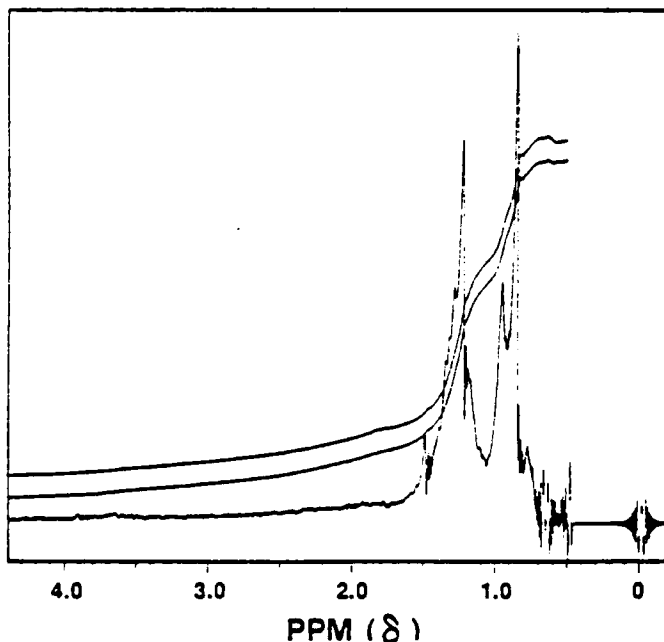


FIG. 1. NMR spectrum of polymethane.

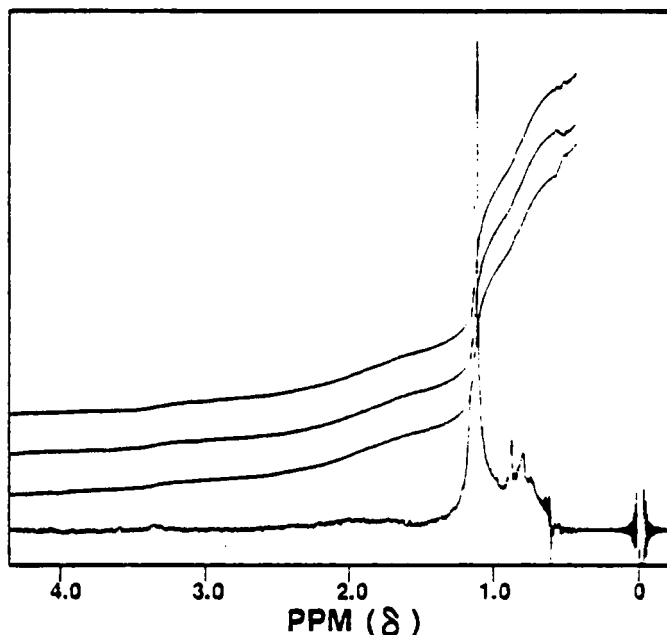


FIG. 2. NMR spectrum of a polymer from methane and propylene.

do indicate that the amount of methane polymerized is 5 to 20 times more when an olefin is added as an initiator (Table 1).

Further evidence for the presence of the block methylene is supported by the presence of a small IR band between 720 and 750 cm^{-1} in the IR spectra of most of the polymeric materials. The CH_2 groups rock in phase at 722 to 785 depending upon the number of CH_2 groups present in the block. The data indicates that methylene groups are present in blocks of different lengths.

The mechanistic implications of the formation of the block methylene are interesting since one must invoke a primary [2] cation to explain it. The formation of this primary cation must involve some extraordinary stabilization by some component in the acid. A proposed mechanism [3] for the polymerization is shown in Scheme 1. The mechanistic scheme involves an attack of a proton on the olefin yielding the primary and secondary propyl cation. This cation (more likely the primary since it is more reactive [2]) then attacks methane to give a pentavalent cation (1) followed by loss of H_2 to give the butyl cation. This is repeated several times, yielding blocks of methylenes which give the 1.25δ peak in the NMR. As evidenced by the NMR spectra of *n*-pentane, *n*-hexane,

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