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Durward T. Roberts JR.[a]; Lawrence E. Calihan[a]
[a] The Central Research Laboratories, The Firestone Tire & Rubber Co., Akron, Ohio

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Polymerization (Polycondensation) of Alkanes over Fluosulfonic Acid and Antimony Pentafluoride

DURWARD T. ROBERTS, JR. and LAWRENCE E. CALIHAN

The Central Research Laboratories
The Firestone Tire & Rubber Co.
Akron, Ohio 44317

ABSTRACT

Several low molecular weight alkanes have been polymerized (polycondensed) over HSO_3F-SbF_5 to yield a highly branched oily oligomer with a molecular weight range from the molecular weight of the monomer to around 700. The order of reactivity for butane and lower molecular alkanes is isobutane > n-butane > propane > ethane > methane. The reactivity is explained by the ease of attack of an acid proton derived from the acid on the alkane sigma bonds as well as the relative stability of the resulting cation formed. A cationic mechanism for this reaction is proposed.

In recent years Olah has published a number of papers on the alkylation and polycondensation of alkanes to various cations and highly branched low molecular weight alkanes. We now report the polymerization (polycondensation) of alkanes to polymeric materials ranging in molecular weight from the monomer to around 700 using HSO_3F-SbF_5 as a catalyst. Olah and his group [1-4] have reported that this strong acid is capable of attacking carbon-carbon and

and carbon-hydrogen sigma bonds in an electrophilic fashion to yield alkyl cations. These reactions included the polycondensation of methane [1, 2] to form t-butyl cation as well as the reactions of nonane and lower alkanes [3] to form various cations and low molecular weight alkanes. It was also reported that alkanes can be alkylated by alkyl cations [4] derived from alkyl fluorides to yield highly branched low molecular weight alkanes. The chemistry of the HSO_3F-SbF_5 interaction and the structure of the active species has been described by Olah [2, 5], Gillespie [6-10], and others [11, 12].

RESULTS

A number of alkanes (methane, ethane, propane, n-butane, and isobutane) have been polymerized to low molecular weight highly branched polyalkanes using HSO_3F-SbF_5 as a catalyst. These polymers or oligomers were obtained by reacting the gaseous alkane with the liquid acid in a stainless steel autoclave at room temperature. The alkane-acid ratio, temperature, and pressure were varied. Gases (C_1 to C_7) remaining in the autoclave after the reaction was over were analyzed by gas chromatography. The polymerization products were isolated by quenching the acid solution with $NaOCH_3/CH_3OH$ at -78°C followed by washing with water. After quenching, monomer and low molecular weight alkanes (C_3 to C_7) were evolved during the warm up from -78°C to room temperature; and the gases were analyzed by gas chromatography. The residue was then extracted with pentane and toluene to crudely fractionate the polymeric material, and the solvents were removed under vacuum to recover the polymeric materials. Products with carbon number C_8 and higher will generally be termed as polymers, while materials C_7 and lower will be termed alkanes. The terminology is a result of the work-up procedure in which the polymer was isolated by removal of the extraction solvents under vacuum. The alkanes that were isolated consisted mostly of propane, butanes, and pentanes. The yield of these alkanes increased when the molecular weight of the monomer increased from methane to n-butane. As shown in Table 1, the yield of polymer also increased with an increase in the molecular weight of the alkane charged. These runs were made at room temperature using two moles of alkane per mole of SbF_5. The acid ratio (ratio of HSO_3F-SbF_5) in these runs was 1 to 1 and the time was 24 hr. Table 2 reveals that the polymerization of n-butane was complete after 6 hr; thus the polymerizations can go to completion in substantially less than 24 hr.

The molecular weight of the products in each polymerization ranged from the molecular weight of the monomer to 700 as evidenced by gas chromatographic data of the alkanes and mass spectra of the polymers. The mass spectra showed peaks at every mass unit from about 100 to 700, the largest peaks being 13 to 15 mass units apart. The average

TABLE 1. Polymerization of Alkanes

Alkane	Wt% of conversion of alkane monomer to polymer[a]
Methane	0.2
Ethane	2.5
Propane	8
n-Butane	15.5
i-Butane	18

[a] Reactions were run at room temperature for 24 hr with a 1:1:2 M ratio of HSO_3F-SbF_5-alkane.

TABLE 2. Yield of n-Butane Polymer vs Time

Time (hr)	Wt% conversion of n-butane monomer to polymer[a]
1	4.5
3	9
6	15
24	15.5

[a] Conditions are the same as in Table 1 except for time.

molecular weight of polybutane was 400 as determined by vapor pressure osmometry. Elemental analysis revealed that a typical polymer contained 70 to 77% carbon, 7 to 10% hydrogen, 4 to 8% sulfur, and only traces of fluorine and antimony, the remainder being oxygen. The carbon-hydrogen ratio indicated that the polymers contained double bonds and/or cyclic rings. These double bonds might have been formed during the work-up ($NaOCH_3/CH_3OH$) by a proton abstraction α to the cation. IR spectra revealed that the sulfur was present in an oxidized form. The NMR spectra of the polymers were examined in detail and an example is shown in Fig. 1, representing polybutane. The spectrum is very complicated but does indicate the presence of a number of different CH_3, CH_2, and CH groups which reveal that the polymer is highly branched in structure. The NMR spectra showed no aromatic protons and small amounts of olefinic protons, indicating that the unsaturation mentioned above comes about either from substituted olefins and/or cyclic components.

The runs were made at 25°C, but running the reactions from 20 to

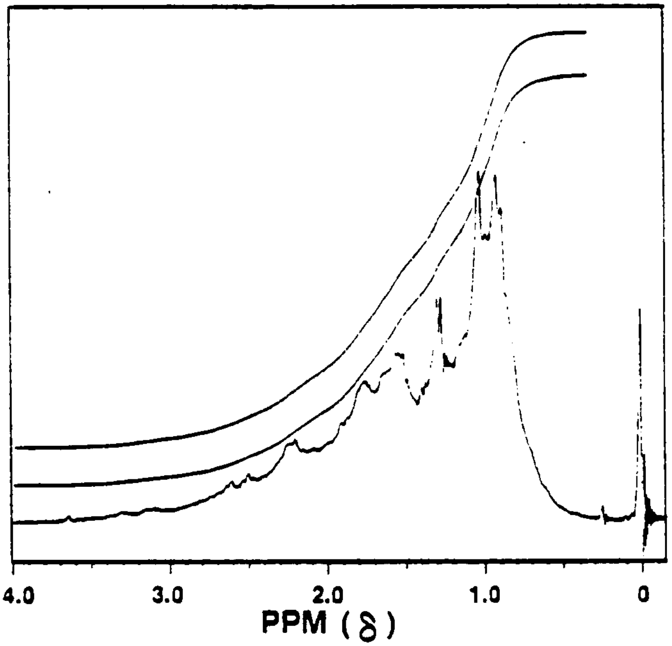


FIG. 1. NMR spectrum of polybutane.

60°C gave similar results, while at temperatures above 100°C little polymer was formed, most of the products being a mixture of C_3 to C_7 alkanes. At 0°C the rate of polymerization was retarded. The rate of the reaction increased with temperature but this was offset by an increase in the breakdown of the polymer by the acid media. Small changes in the acid ratio did not significantly affect the polymerization reaction.

During the polymerization reaction a competitive reaction, that of cleaving the alkane monomer to lower molecular weight alkanes, was also taking place. The relative amount of cleavage depended upon the monomer; for example, there were more cleavage products when n-butane was used as a monomer than when isobutane was used. This observation agrees with Olah's results [3] since the most favorable cleavage reaction for isobutane is that of the tertiary carbon-hydrogen yielding a t-butyl cation and hydrogen, whereas the most favorable cleavage for n-butane is carbon-carbon scission yielding an ethyl cation and ethane.

The composition of the gaseous alkanes in the autoclave during an n-butane polymerization was followed versus time. The results are

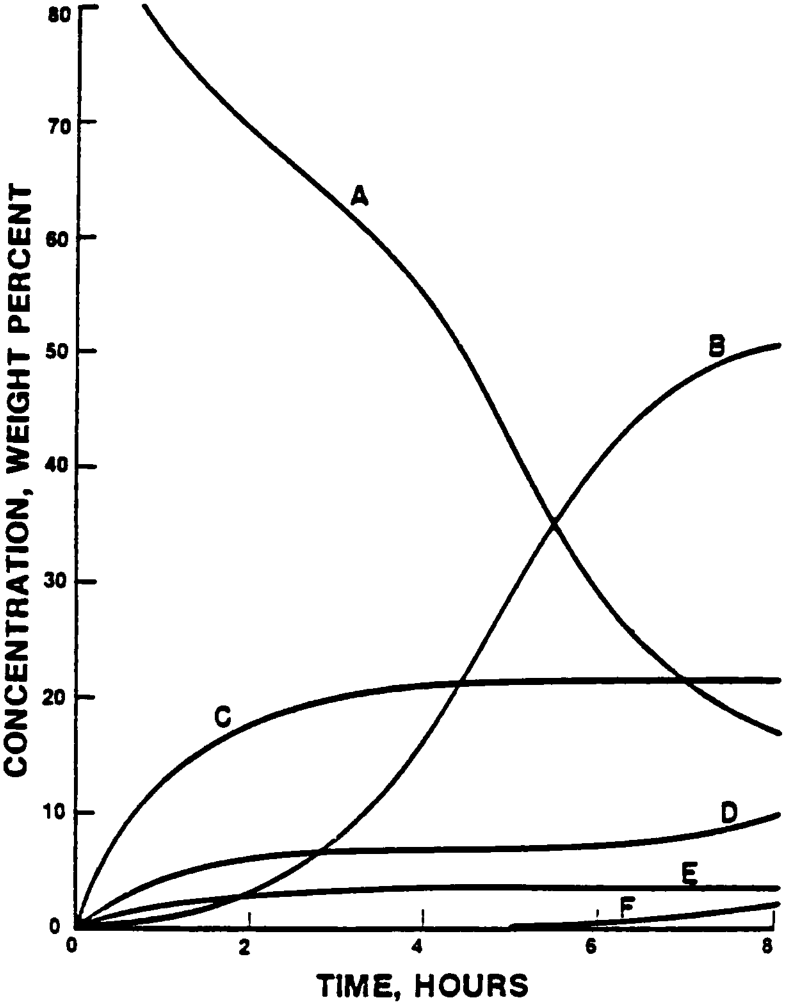


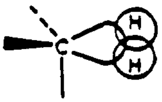
FIG. 2. Hydrocarbon concentration of the gases above the HSO_3F-SbF_5 catalyst for a polymerization using n-butane gas as the monomer. (A) n-Butane, (B) i-butane, (C) ethane, (D) propane, (E) methane, and (F) pentanes.

shown in Fig. 2. The figure reveals that there was a large initial formation of ethane along with smaller amounts of methane and propane. Each of these concentrations leveled off after the first 2 hr. The isobutane concentration did not increase rapidly until after 3 hr. At 5 hr small amounts of pentanes and hexanes appeared. All of the butane monomer was accounted for either as polymer in the acid phase or as alkane in the gaseous phase (15.5% polymer).

When other low molecular weight hydrocarbons were reacted with the acid, varying amounts of alkanes from methane to heptane were observed in the gas phase. n-Butane and propane were formed along with the polymer when isobutane was used as a monomer. The yields of the various alkanes depended upon the time of reaction (e.g., after 24 hr around 25% of the unreacted isobutane was converted to propane and 10% was isomerized to n-butane). When propane was reacted with the acid media only ethane (10% yield after 24 hr) and polymer were formed in reasonable yield. When methane or ethane were polymerized, the polymer was formed in low yield and only traces of other alkanes were produced.

DISCUSSION

The results can be explained utilizing the same reasoning used by Olah and his group [1-4]. They invoked a protolytic attack on the hydrogen-carbon or carbon-carbon sigma bonds to give a three-center sp^3 hybridized penta-coordinated carbonium ion and suggested Structure 1 to be the carbonium ion intermediate. Hereafter, Structure 2 will be used to represent Structure 1. This type of structure was chosen from self-consistent field calculations [2] and direct observation of the chemistry of methane in super-acid. Hogeveen [13] has proposed a slightly different intermediate cation in the $HF\text{-}SbF_5$ system.



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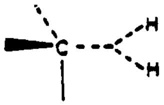

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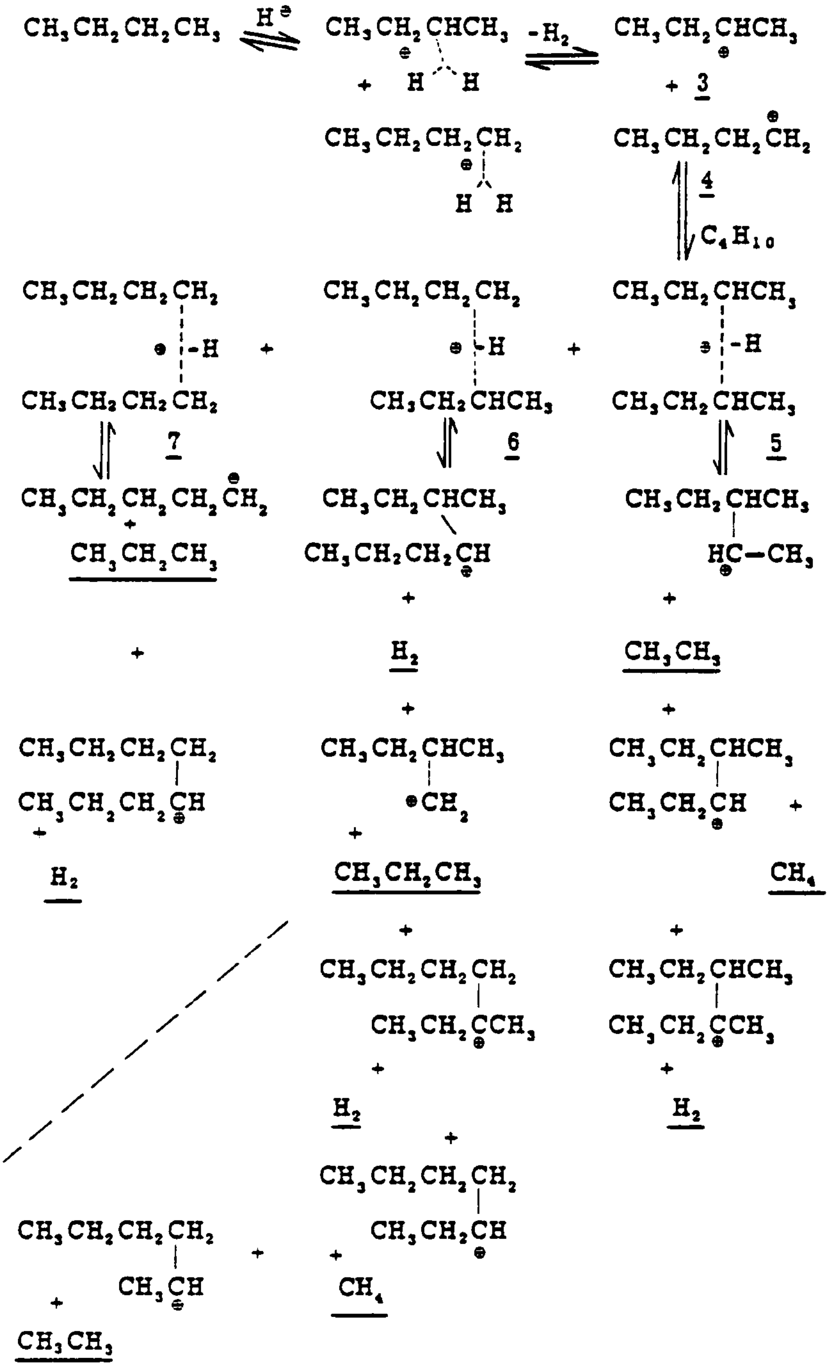
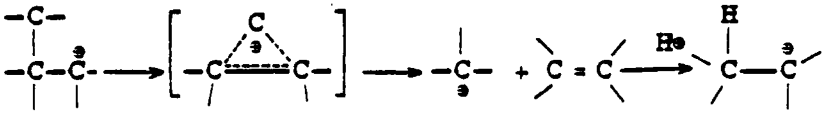
The following mechanism is being proposed by the authors to account for the observed results. The proposed mechanism for the polymerization of n-butane is outlined in Scheme 1 and is described as follows:



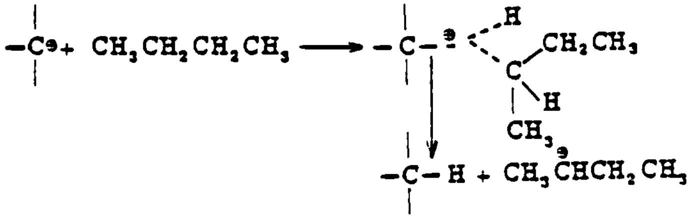
SCHEME 1.

The n-butane or other hydrocarbons can be protonated to produce a pentavalent carbonium ion which in turn loses hydrogen to give the corresponding cations 3 and 4. These ions can then attack another molecule of n-butane to give the pentavalent ions 5, 6, and 7. The latter ions cleave to give H_2, CH_4, C_2H_6 or C_3H_8, and new cations (this mechanism accounts for the formation of the alkanes which were observed early in the run). These newly formed cations can then continue to react with more molecules of n-butane to eventually form polymeric materials.

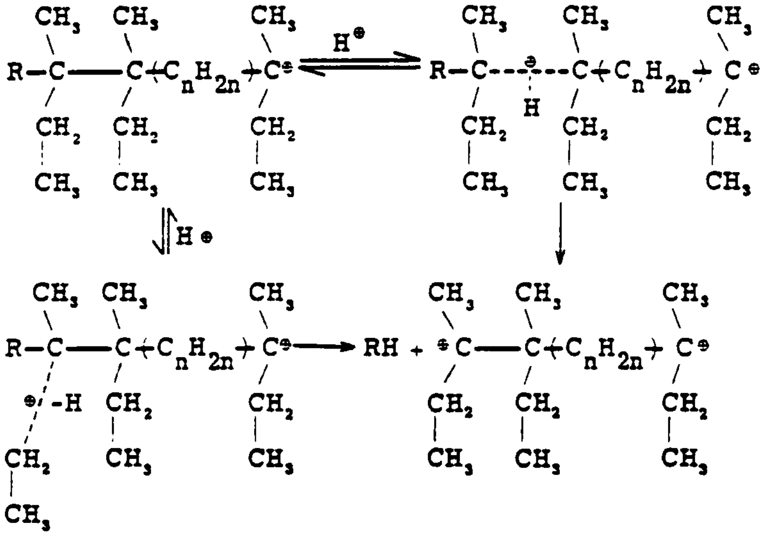
As discussed earlier in the paper, the average molecular weight of the polymer is around 400. Several mechanisms can be proposed to account for this. First, a β-cleavage can take place during the polymerization as shown in Scheme 2. Second, a hydride transfer [14], from the monomer to a propagating cation can take place as shown in Scheme 3. Third, multiple cations could be formed by attack of HSO_3F-SbF_5 on the polymer molecule at a position away from the propagating cation which would cause a cleavage of the molecule. Two examples are shown in Schemes 4 and 5. Fourth, the polymer cation could combine with a counteranion (e.g., SO_3F^-). Each of the above routes would have the effect of reducing the molecular weight of the polymer. The former three would involve chain transfer-type mechanisms which would generate new cationic centers while the latter would terminate the polymerization. There is no experimental evidence for the first three proposed mechanisms. Evidence for the latter is found in the elemental analysis which reveals the presence of sulfur in the polymer. The reactions of counteranions with polymer cations do not add fluorine to the polymer because during work-up the sulfur-fluorine bond is hydrolyzed, and the propagating cations are not likely to react with the fluoride ions since they are poor nucleophiles.



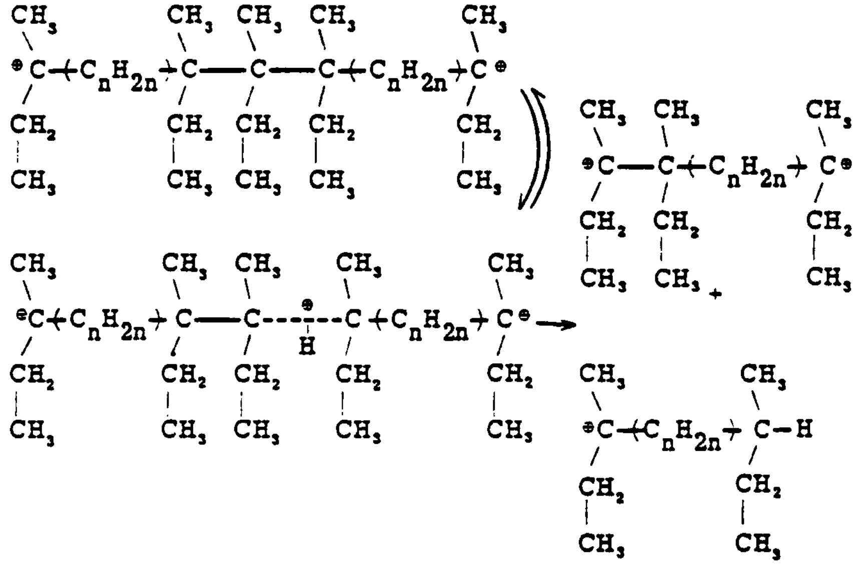
SCHEME 2.



SCHEME 3.



SCHEME 4.



SCHEME 5.

When high molecular weight polyisobutylene and polyethylene are treated with the acid under the same conditions, they go to the same type of highly branched low molecular weight polymeric material. The NMR, mass spectra, and color appear to be very similar to those of the polyalkanes, indicating the polymeric materials are similar in structure (branched) and molecular weight to the polyalkanes. This might indicate that thermodynamic equilibrium conditions are attained in the acid medium.

Thermodynamic calculations provide further evidence for the polymerization mechanism by revealing that a polymerization involving the forming and breaking of carbon-carbon bonds to yield low molecular weight alkanes (e.g., methane) is more favorable than a polymerization involving the carbon-hydrogen bond to yield hydrogen. Table 3 gives an example of these reactions when n-butane is the monomer. The dimerization of n-butane giving n-octane and hydrogen has a +12 kcal/mole free energy of reaction while the dimerizations (disproportionations) yielding pentane, hexane, or heptane, as well as the lower molecular weight alkanes methane, ethane, and propane, have approximately a 0 kcal/mole free energy of reaction. Since the latter three reactions (Table 3) have a more negative free energy of reaction, they should be the more favorable pathway to the formation of polymer along with accompanying formation of lower molecular weight alkanes.

The addition of hydrogen [13, 15-17] to a butane polymerization had the effect of increasing the production of CH_4, C_2H_6, and C_3H_8 and decreasing the production of polymer. Evidently it suppressed the loss of hydrogen from the protonated monomer and caused instead the loss of alkanes.

In Olah's work an excess of acid was used, whereas in our work we used an excess of alkanes. Using the excess alkane allowed the cations that were formed in the acid to react with the additional alkane present and form polymeric materials.

TABLE 3. Thermodynamics of Polymerization

Reaction (gas phase)	ΔF° RCN at room temperature in (kcal/mole)
$2n\text{-}C_4^\circ \rightarrow n\text{-}C_8^\circ + H_2$	+12
$2n\text{-}C_4^\circ \rightarrow n\text{-}C_7^\circ + C_1^\circ$	-2
$2n\text{-}C_4^\circ \rightarrow n\text{-}C_6^\circ + C_2$	+0.3
$2n\text{-}C_4^\circ \rightarrow n\text{-}C_5^\circ + C_3^\circ$	+0.5

EXPERIMENTAL SECTION

General

Mass spectra were recorded on an Associated Electrical Industries Ltd. MS-12 mass spectrometer, and IR spectra on a Perkin-Elmer No. 137 spectrometer. NMR spectra were recorded on a Varian DA 610 NMR spectrometer. CCl_4 and $CDCl_3$ were used as solvents and TMS as the internal standard. The gas chromatographs were run on a 15-ft column consisting of 20% DMS supported on 45/60 chromosorb P. The alkanes were purchased from Matheson Gas Products and dried by passing them through molecular sieves. Antimony pentafluoride and fluosulfonic acid were purchased from Alpha and Allied, respectively, and distilled before use.

Polymerization in a 300-ml Autoclave [2]

In a dry box under nitrogen, 1.7 ml of SbF_5 (0.023 moles, 5.0 g) and 1.3 ml of HSO_3F (0.023 moles, 2.3 g) were added to a 50-ml flask (either Pyrex or Teflon) with a stirrer. The flask was placed in the autoclave and the autoclave sealed, flushed, and pressured to the desired level with the hydrocarbon (2 moles alkane per mole of acid). Time, temperature, and pressure were varied. After the polymerization, gas chromatographs of the gases above the acid catalyst were taken, the autoclave was vented, and the quenching procedure begun.

Quenching Procedure

When the reaction was complete, the reaction vessel was removed from the autoclave and cooled to -78°C and quenched with 30 ml of saturated $NaOCH_3$ solution. The mixture was warmed to room temperature and, if necessary, neutralized with NH_4OH. Any gases evolved during warm up were analyzed by gas chromatography. The polymer was extracted from the media with pentane or toluene and washed with water. Removal of the solvent left a tan-to-red color oily polymeric material; IR (neat) 2950, 2880, 1460, and 1380 (CH) and small peaks at 1200 to 1050 and 900 to 700 cm^{-1} (S-O): mass spectrum (70 eV) peaks at every mass unit up to and including 700, highest peaks were 13 and 15 units apart.

Analysis: Found (av): C, 70-77; H, 7-10; N, O; S, 8-4; Sb, 0.03-0.01; F, 0.5-0.1.

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REFERENCES

[1] G. A. Olah and R. H. Schlosberg, J. Amer. Chem. Soc., 90, 2726 (1968).

[2] G. A. Olah, G. Klopman, and R. H. Schlosberg, Ibid., 91, 3261 (1969).

[3] G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, Ibid., 93, 1251 (1971).

[4] G. A. Olah and J. A. Olah, Ibid., 93, 1256 (1971).

[5] A. Commeyras and G. A. Olah, Ibid., 91, 2929 (1969).

[6] R. J. Gillespie, J. B. Milne, and J. B. Senior, Inorg. Chem., 5, 1233 (1966).

[7] R. J. Gillespie, K. Ouchi, and G. P. Pez, Ibid., 8, 63 (1969).

[8] R. C. Thompson, J. Barr, R. J. Gillespie, J. B. Milne, and R. A. Rothenbury, Ibid., 4, 1641 (1965).

[9] J. Bacon, P. A. W. Dean, and R. J. Gillespie, Can. J. Chem., 48, 3413 (1970).

[10] J. Barr, R. J. Gillespie, and R. C. Thompson, Inorg. Chem., 3, 1149 (1964).

[11] R. C. Thompson, in Inorganic Sulfur Chemistry (G. Nickless, ed.), Elsevier, New York, 1968, Chap. 17.

[12] C. J. Hoffman, B. E. Holder, and W. L. Jolly, J. Phys. Chem., 62, 364 (1958).

[13] H. Hogeveen. C. J. Gaasbeck, and A. F. Bickel, Rec. Trav. Chim. Pays-Bas, 88, 703 (1969).

[14] P. D. Bartlett et al., J. Amer. Chem. Soc., 66, 1531 (1944).

[15] H. M. Buck et al., Tetrahedron Lett., 1964, 2987.

[16] A. F. Bickel et al., Chem. Commun., 1967, 634.

[17] H. Hogeveen and A. F. Bickel, Rec. Trav. Chim. Pays-Bas, 86, 1313 (1967).

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