Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Kennedy, J. P. , Melby, E. and Johnston, J.(1974) 'An Attempt to Adapt Superacid Chemistry for "Living" Carbenium Ion Polymerizations', Journal of Macromolecular Science, Part A, 8: 3, 463 — 468

To link to this Article: DOI: 10.1080/00222337408065843

URL: http://dx.doi.org/10.1080/00222337408065843

J. MACROMOL. SCI.—CHEM., A8(3), pp. 463-468 (1974)

An Attempt to Adapt Superacid Chemistry for "Living" Carbenium Ion Polymerizations

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ABSTRACT

The discovery that carbocations can be stabilized in super acid media, e.g., SbF_5-SO_2, etc., raises the possibility of "living" carbenium ion polymerization. Polymerization experiments with isobutylene and styrene carried out at high acid concentrations and in the virtual absence of nucleophile, i.e., under conditions conducive for living polymerization, failed to indicate a linear conversion vs molecular weight relationship and/or block copolymer formation. Additional model experiments with 2,4,4-trimethyl-1-pentene substantiate our conclusions that "living" carbocation polymerizations are unlikely to be produced by superacid chemistry.

INTRODUCTION

"Living" carbenium ion polymerization is still an unattained, challenging problem mainly because of the intrinsically unstable nature of the propagating species. Relatively low carbenium ion stability (high reactivity) leads to relatively high rates of chain transfer and, consequently, to low and largely unpredictable molecular weight polymers. Olah's significant discovery that elusive carbenium ions can be stabilized and subjected to direct observation in SbF_5-SO_2, SbF_5-SO_2ClF, superacid media [1] interested us to explore the possibility of producing propagating but noneliminating (nontransferring) carbocations and thus obtain "living" carbenium ion polymerizations.

According to observations made prior to the advent of superacid chemistry, SbF_5, when used in catalytic amounts, behaves as a conventional strong Lewis acid and polymerizes isobutylene to fairly high molecular weight products [2]. We examined in detail the possibilities of adapting superacid chemistry to polymer synthesis. On the basis of available information [1, 3], we theorized that to produce "living" carbenium ion polymerizations we have to work essentially in the absence of monomer (nucleophile) in excess antimony pentafluoride. This paradoxical requirement arises because olefin monomers are nucleophiles in carbocation polymerization and as such may abstract protons from the propagating species. The presence of excess acid is necessary to stabilize the carbenium ion.

Another requirement is the homogeneity of the system. Nonpolar olefin polymers carrying a propagating ion pair terminus combine totally dissimilar solubility characteristics in one molecule and therefore cannot be dissolved in SO_2 or SO_2ClF used in superacid chemistry.

To overcome these experimental difficulties we slowly distilled monomer (isobutylene) into well-stirred superacid systems (SbF_5) in solvents of low nucleophilicities [1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113), CH_3Cl, CH_2Cl_2] in the range -30 to -115°C; however, the bulk of the experiments were carried out at -50°C.

Diagnostic probes to demonstrate "living" polymerization are 1) a linear ascending plot of monomer conversion vs molecular weight and 2) the synthesis of block copolymers by introducing a second Monomer B to a completely polymerized charge of Monomer A.

RESULTS AND DISCUSSION

Results of a representative series of experiments in which isobutylene was distilled slowly into a concentrated solution of SbF_5 in Freon 113 are summarized in Table 1. Final molecular weights (low molecular weight oils) were obtained at lowest conversions, and further monomer addition did not change this level. Subsequent

TABLE 1. Conversions and Number-Average Molecular Weights Obtained by Adding Isobutylene to SbF_5 (0.13 mole/liter) in Freon 113 at -30°C

Sample No.	Grams isobutylene added	Conversion (%)	$\overline{M}_n$
1	1.8	9.1	572
2	6.0	30.0	570
3	7.2	36.4	597
4	8.4	42.4	535
5	9.6	48.5	564
6	10.8	54.5	589
7	15.0	75.8	564
8	19.8	100.0	665

to isobutylene addition, styrene was introduced into the quiescent system. The reaction was quenched by the addition of prechilled methanol, and the mixture was repeatedly extracted with n-pentane (good solvent for polyisobutylene, nonsolvent for polystyrene). The IR spectra of the extracts did not indicate the presence of polystyrene. Similarly, the residue was free of polyisobutylene (by IR). Thus selective extraction gave no evidence for block copolymer. Similar results were obtained using methyl chloride, methylene chloride, and n-pentane diluents for the polymerization.

Neither did the polymerization of styrene with SbF_5 in different solvents give any indication of "living" cationic polymerization. This is in agreement with the finding that the parent styryl cation is unstable even in superacid media [4].

In sum, in none of the systems studied did we obtain any experimental indication of "living" cationic polymerization.

The results of these polymerizations have been examined in the light of theories and experiments reported in the literature. The following facts have to be taken into consideration in trying to explain our observations: First of all, stable alkyl carbenium ions containing more than eight carbon atoms have never been observed in superacid media. Indeed, the dimethyl neopentyl carbenium ion, i.e., the dimer in isobutylene polymerization, is known to crack to the trimethyl carbenium ion even at -80°C [3, 5, 6]. Brouwer and Hogeveen reported that the equilibrium constant for β-cleavage in strong protonic acid media is of the order of 10^8 moles/liter, consequently cracking is favored in the presence of excess acid [7].

Abstraction of secondary and tertiary hydrogen atoms from alkanes using SbF_5 occurs even at -100°C, and primary hydrogen atoms can be abstracted at -50°C [8, 9]. (The exact mechanism of hydride abstraction with SbF_5 is a matter of controversy. In our systems, hydride abstraction from a polymer backbone results in the same degradation processes regardless of the mechanism.) Thus it may be anticipated that in a polymerization, hydride abstraction from the polymer backbone would result in undesirable reactive carbenium ions leading to a variety of ill controlled inter- and intramolecular reactions, e.g., hydride transfer, alkylation, isomerization, branching, and/or cleavage [11]. The occurrence of any or all of these reactions in a cationic polymerization can explain the production of ill-defined, low molecular weight polymers.

These thoughts are substantiated by the following facts: Polyethylene and paraffin wax degrade in FSO_3H-SbF_5, resulting in the trimethyl carbenium ion end product [5]. When we dissolved 0.1 g polystyrene ($\overline{M}_w = 126{,}000$, $\overline{M}_w/\overline{M}_n = 1.1$) in a 20.0 ml solution of SbF_5 (1.6×10^{-2} M) in methylene chloride at -50°C, a gel was obtained. Gelation is probably due to cross-linking by alkylation of the aromatic rings by carbenium ions generated along the polymer backbone. When high molecular weight polyisobutylene (Oppanol B 200) was dissolved in a 5.5×10^{-2} M solution of SbF_5 in pentane and methylene chloride (1:1) at -50°C, degradation occurred as indicated by a reduction in the intrinsic viscosity. Furthermore, after a sample of polyisobutylene was treated with SbF_5 at room temperature for 30 min, PMR showed the exclusive formation of trimethyl carbenium ion in the liquid fraction.

To further substantiate our conclusions, we undertook model studies using 2,4,4-trimethyl-1-pentene which cannot polymerize beyond the dimer because of steric hinderance. By following the reaction of this olefin and SbF_5, we hoped to find evidence for stable C_8, C_{12}, and C_{16} carbenium ions corresponding to the early stages of an isobutylene polymerization. The slow, stepwise addition of 2,4,4-trimethyl-1-pentene to well-stirred solutions of SbF_5-SO_2 at -78°C and SbF_5-SO_2ClF at -120 and -78°C was followed by PMR spectroscopy. The mixtures resulting from these reactions were quenched by pouring the solutions into ice water, neutralizing with Na_2CO_3 and extracting with ether. In each case, when small amounts of 2,4,4-trimethyl-1-pentene were added to the SbF_5 solutions, the PMR spectrum showed the initial formation of trimethyl carbenium ion. As more olefin was added, the resonance characteristic of trimethyl carbenium ion disappeared and a complicated PMR spectrum remained which did not contain downfield peaks characteristic of stable carbenium ion centers. The PMR spectra of the products recovered from the quenching experiments were very complex, indicating a mixture of products. The IR spectra showed stretching bands characteristic of olefins and alcohols. Gas chromatographic analysis of the mixtures showed a minimum of ~50 products.

These results with 2,4,4-trimethyl-1-pentene reinforce our conclusions in regard to our polymerization studies. The presence of olefins and the absence of stable carbenium ions in the reaction mixture of 2,4,4-trimethyl-1-pentene with SbF_5 indicate chain transfer. The complexity of the mixtures demonstrates the extent of undesirable side reactions discussed earlier.

CONCLUSION

The use of SbF_5 in the high concentrations needed for the stabilization of carbenium ions results in ill-defined low molecular weight polymers. Carbenium ions are stable only in the absence of nucleophilic agents; however, as propagation proceeds, the polymer, a nucleophile, is produced which is susceptible to attack by both the strong acid and the growing carbenium ions. For these reasons, well-defined "living" polymers are not likely to be obtained by the use of superacids.

ACKNOWLEDGMENTS

The authors wish to thank the Firestone Tire and Rubber Company for supporting this research, and Dr. G. A. Olah for helpful comments and suggestions.

REFERENCES

[1] G. A. Olah, E. Baker, J. Evans, W. Tolgyesi, J. McIntyre, and I. Bastein, J. Amer. Chem. Soc., 86, 1360 (1964). G. A. Olah, Science, 168, 1298 (1970). G. A. Olah, Angew. Chem., Int. Ed., 12, 173 (1973).
[2] W. C. Smith and R. M. Thomas, U.S. Patent 2,734,047 (1956).
[3] D. M. Brouwer, Rec. Trav. Chim. Pays-Bas, 87, 210 (1968).
[4] G. A. Olah, R. D. Porter, and D. P. Kelly, J. Amer. Chem. Soc., 93, 464 (1971).
[5] G. A. Olah and J. Lukas, Ibid., 89, 4739 (1967).
[6] G. A. Olah and Y. Halpern, J. Org. Chem., 36, 2354 (1971).
[7] D. M. Brouwer and H. Hogeveen, Rec. Trav. Chim. Pays-Bas, 89, 211 (1970).
[8] G. A. Olah, J. Amer. Chem. Soc., 94, 808 (1972).

[9] J. Lukas, P. A. Kramer, and A. P. Kouwenhove, Rec. Trav. Chim. Pays-Bas, 92, 44 (1973).

[10] G. A. Olah and J. A. Olah, J. Amer. Chem. Soc., 93, 1256 (1971).

Accepted by editor July 17, 1973
Received for publication August 21, 1973