

Studies on the Oxocarbenium Polymerization of Tetrahydrofuran Initiated by Chlorinated Hycar Polymers in Conjunction with AgBF_4

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ABSTRACT

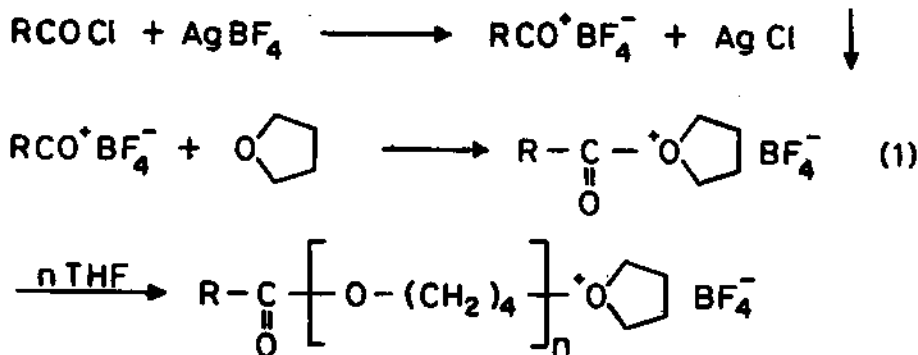
Cationic polymerization of tetrahydrofuran was initiated by chlorinated carboxyl terminated polybutadiene and butadiene-acrylonitrile copolymer in conjunction with AgBF_4 . Simultaneous crosslinking was observed in all cases. This was attributed to the various chemical reasons.

INTRODUCTION

It is well known^{1,2} that *in-situ* formation of oxocarbenium salt and cationic polymerization can be achieved by reacting an acid chloride with a stoichiometric amount of silver salt in the presence

of appropriate monomer. Taking tetrahydrofuran (THF) as a typical cationic susceptible monomer, the overall polymerization sequence would be represented by equation (1).

The type of the initial acid chloride affects the structure of the resultant polymer. Functional



polymers³, block and graft copolymers² may be prepared by the appropriate choice of the acid chloride. As a general application of this method, we have recently demonstrated^{4,5} the possibility of preparing block copolymers by combinations of cationic and radical routes in two different sequences. Carboxyl terminated reactive liquid polymers have been extensively used to improve impact and crack resistance of epoxy resins⁶. The role of diacid functionality was important in these reaction mechanisms involving Hycar polymers and epoxy resin in the presence of piperidine as a curing agent. Therefore it seemed appropriate to use this diacid functionality in the usual acid chloride-silver salt technique for the polymerization of THF and thus improve the rubbery property of poly THF.

EXPERIMENTAL

Materials. Hycar CTB 2000×162 (carboxyl terminated polybutadiene, $\bar{M}_n = 4200$, functionality: 1.9), Hycar CTBN 1300×8 (carboxyl terminated butadiene-acrylonitrile copolymer, $\bar{M}_n = 3600$, functionality: 1.8, acrylonitrile content: 18%), and Hycar CTBN 1300×9 ($\bar{M}_n = 3600$, functionality: 2.4, acrylonitrile content: 18%), gifts from B.F. Goodrich were used without further purification.

THF was purified by the conventional drying and distillation procedures. *Cis* butadiene rubber (CBR Petkim 1203) was dissolved in THF and reprecipitated in distilled water before use.

Chlorination of Hycar Polymers. A solution of approximately 1.0 g Hycar polymer in 20 mL of dry benzene was chilled in an ice bath and treated with excess PCl_5 . Stirring was continued for a few minutes at ice temperature and the solution was left at room temperature overnight. The color of the solution became brownish. The solution was then filtered and evaporated to a paste. Phosphorus oxychloride was removed by reduced pressure evaporation at room temperature.

Polymerization Procedure. Appropriate solutions of chlorinated Hycar polymers and AgBF_4

in THF were degassed in the usual manner. Polymerization and recovery of the polymer were carried out as described previously^{4,5}.

RESULT AND DISCUSSION

Cationic polymerization of THF in bulk was achieved by utilizing chlorinated Hycar CTB in the presence of AgBF_4 at room temperature. Typical data for the polymerization is given in Table I.

TABLE I. Polymerization of THF with Chlorinated CTB in Conjunction with AgBF_4 at Room Temperature

RCOCl [M] × 10 ³	AgBF ₄ [M] × 10 ³	Conversion, %	Composition of the polymer,* % THF
9	205	1.59	68
18	36	9.31	47
37	72	17.25	80
124	248	20.31	91

*Calculated from elemental analyses.

The most interesting feature of these polymers is their ability to form spontaneous gels as soon as the polymerization starts. This behavior was observed with all the three types of Hycar polymers used in the system. Various chemical reasons can be given to explain the formation of insoluble polymers. Franta and co-workers² claimed that if the functionality of the initiator was more than two, specific reactions are evidenced in the latter steps of polymerization, which lead to crosslinking.

In our studies it is probable that the functionality of the initial polymers are increased by further chlorination of unsaturated bonds present in the backbone of the polymer. Determination of chlorine content indicated that 3% of Hycar CTB polymer was chlorinated during the reaction with PCl_5 in benzene. Secondary alkyl halides are known to initiate cationic polymerization of THF with silver salts in a similar manner. It was

also suggested by Franta and co-workers that crosslinking may be prevented by slowing down the whole process by working at temperatures below 10°C. In this study even at these low temperatures crosslinked polymers were formed although overall rate of polymerization was considerably decreased.

To propose a tentative explanation of the causes of this gel formation, further information can be reduced from the addition of high molecular weight *cis* butadiene rubber, which has the same backbone but no functionality, in an independent acid chloride-silver salt initiating system. For this purpose THF was polymerized by using azobiscyano pentanoyl chloride in conjunction with AgBF₄ in the presence of CBR at room temperature. Immediate crosslinking of the CBR was observed with concomitant precipitation

of AgCl. This behavior favors the hypothesis that the active centers react with the double bonds present in the Hycar polymers. Thus crosslinking occurs as follows:

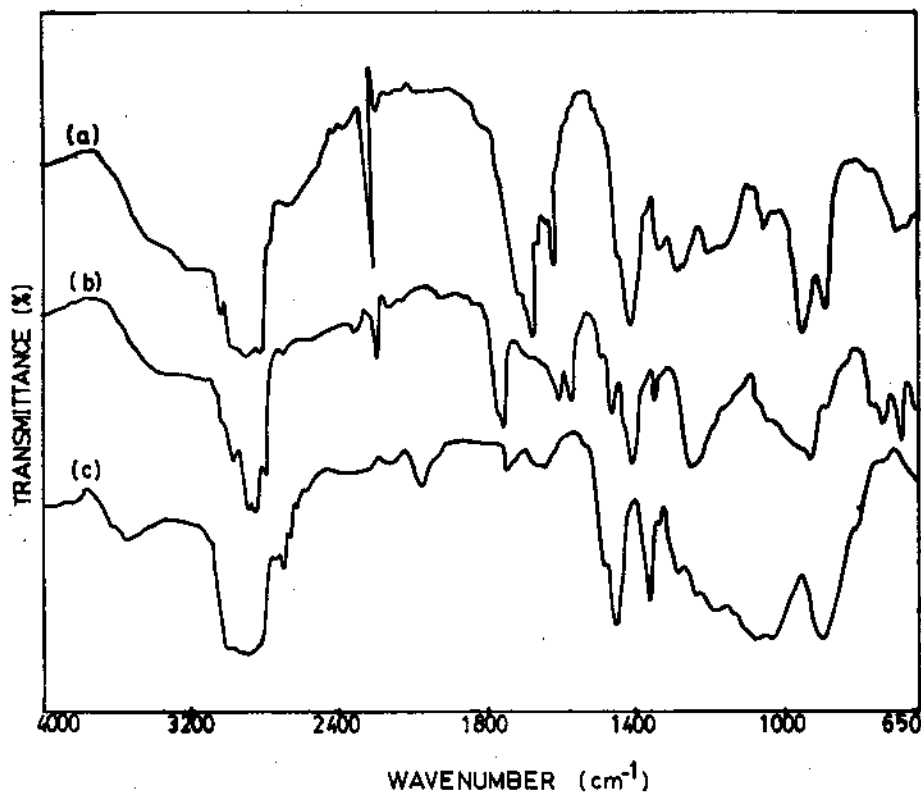
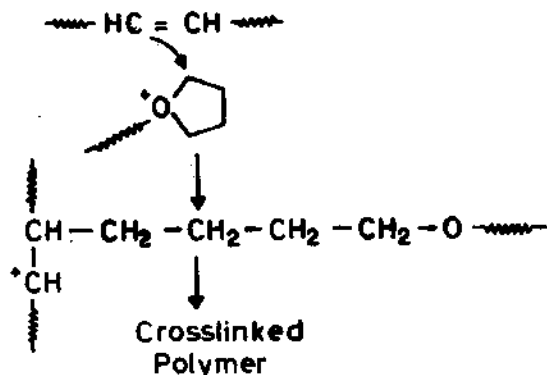


Fig. 1. Infrared spectra of (a) CTBN, (b) chlorinated CTBN, and (c) spectra of the copolymer.

Similar results were obtained from Hycar CTBN polymer. One interesting point is the disappearance of the sharp band at 2200 cm^{-1} corresponding to the CN group in the IR spectrum of the crosslinked polymer (Fig. 1). This indicates the possible interactions of strongly nucleophilic CN groups with growing oxonium ions during the polymerization process. The infrared spectra of the crosslinked polymer showed an absorption peak at 1730 cm^{-1} and 1100 cm^{-1} characteristic of an ester carbonyl and C—O ether bond respectively in addition to Hycar CTBN peaks. In conclusion, the preliminary results reported here confirms the applicability of acid chloride-silver salt initiating system to Hycar polymers. But interactions between initiating or propagating

active centers and functional groups present in the polymer chains as are clear from the gelation in all cases, are deterrent to the use of the method.

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