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PREPARATION AND REACTIONS OF POLYTETRAHYDROFURAN WITH ACRYLATE END GROUP

Akrilat Uc Grubu İçeren Politetrahidrofuranın Eldesi ve Reaksiyonları

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Key words: *Polymerisation, Polytetrahydrofuran*

SUMMARY: Polytetrahydrofuran with acrylate end group was prepared by polymerizing tetrahydrofuran utilising acryloylchloride–$AgBF_4$ combination. Possibilities of chain extension and graft copolymerization were discussed.

ÖZET: Akrilat uc grubu içeren politetrahidrofuran; akriloilklorür-$AgBF_4$ karışımı kullanılarak, tetrahidrofuranın polimerleştirilmesiyle elde edilmiştir. Zincir uzatma imkânları ve aşı kopolimerleşmesi tartışılmıştır.

INTRODUCTION

Significant advances have been made to prepare block and graft copolymers with known structures. This is often achieved by preparing a polymer with a functional end group capable of acting as an initiator or monomer and thus producing active sites for second block.

Bamford et. al.[1] attached photochemically active dibenzazepine units to the polymers which may then be chain extended or copolymerized, when irradiated at appropriate wave lengths. Polystyrene/polymethylmethacrylate block copolymers were prepered[2] utilising bromine terminated polystyrene. Polymers with carboxyl or OH groups as the terminal groups can provide rubbery link in condensation polymers and have potential application in polyurethane technology[3]. In another study[4], polymerizable acrylate and methacrylate end groups incorporated to polytetrahydrofuran using protic initiators and the corresponding carboxylic acid anhydride as transfer agent.

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On the other hand, oxorcarbenium salts ($R-C\equiv O^+ X^-$) with appropriate anions are efficient initiators for the tetrahydrofuran polymerization. These salts can be prepared[5], in situ, by a reaction between acid halides and stochiometric amount of silver salt such as $AgBF_4$ accordig to:

$$R-COCl + AgBF \longrightarrow RCO^+ BF^- + AgCl \qquad (1)$$

These studies led us to prepare polytetrahydrofuran with functional end group by using acryloylchloride as acid halide in this initiation system.

EXPERIMENTAL

Materials

THF(Fluka), purified as described previously[6]. Acryloylchloride (Fluka) kept under vacuum and distilled befor use. Styrene, methylmethacrylate purified by conventional methods.

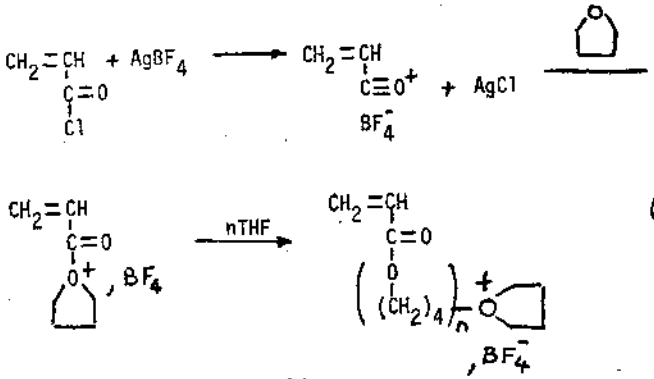
Polimerization Procedure

Bulk THF was distilled on to the reaction vessel containing given amount of $AgBF_4$ using vacuum line method. Addition of acryloylchloride in vacuum system by distillation, causes immediate precipitation of white AgCl, Polymerisation started spontaneously whilst degassing and rapid increase in solution of poly-THF was precipitated into cold water containing a little amount of base after filtering off traces of AgCl.

RESULTS AND DISCUSSION

The synthesis of poly THF with acrylate end group was achieved by using bulk polymerisation of THF with acryloyl chloride, $AgBF_4$ combination as following sequence of reactions.

In a typical polimerization reaction, 2×10^{-2} M acryloyl chloride and 2×10^{-2} M $AgBF_4$ in THF at room temperature produced 34 % yield of poly THF after 30 minutes. IR spectra of the obtained polymer is shown in Figure I. Absorption peak at 1725 cm^{-1} characteristic of an ester carbonyl indicates acrylate end group.



(2)

Figure 1

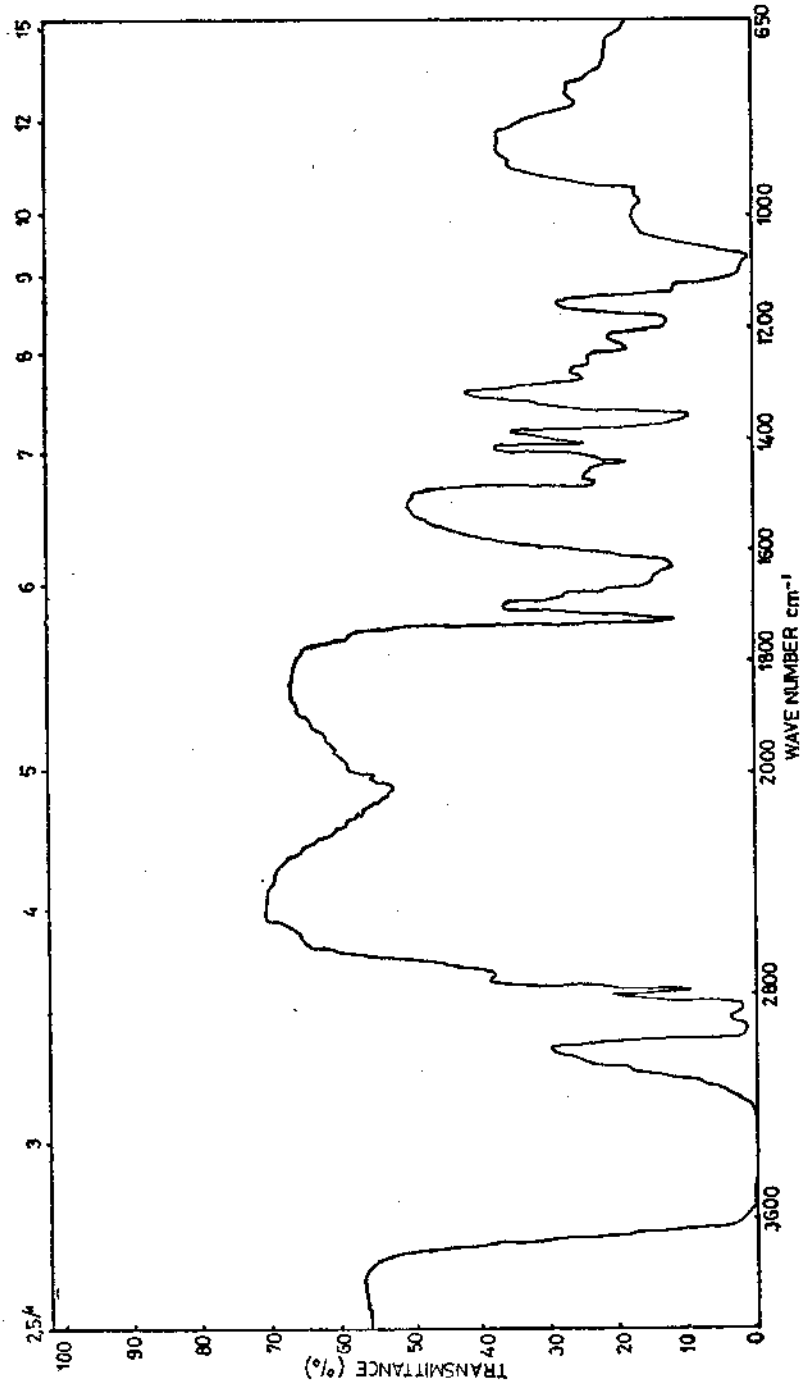
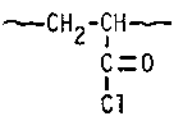
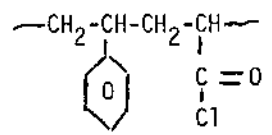
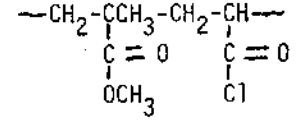


Figure 1 A. IR spectra of polytetrahydrofuran with acrylate end group

TABLE I

Polymerization of THF (bulk) with polymeric acyl chloride in the presence of $AgBF_4$ at room temp.

Polymer	Structure	Crosslinking
polyacryloylchloride		+
polystyrene co-acryloylchlrode		+
poly methylmethacrylate-co-acryloylchloride		+

For the initiation of oxocarbenium polimerization, addition mechanism was purposed in previous studies[5]. We have used several polymers having acyl chloride functionality in polymer backbone as co-initiator with $AgBF_4$ for the polymerization of THF (Table I). In all cases formation of crosslinking was observed even at early stages of polymerisation. This is another evidence for the validity of addition mechanism of initiation since initiating sites are formed on the initial polymer chains. Crosslinking efficiency increased by the number of acyl groups on the initial backbone.

Furthermore, acrylate ended polyTHF was subjected to chain extension and grafting reactions with vinyl type monomers. For the forme purpose, 120 mg. polyTHF (η=0,46) in 2 ml THF containing 20 mg. dibenzoyl peroxide was kept at 60 °C for 2 hours. At the end of reaction, polymer was precipitated in water (η=0,14). Decrease in the solution viscosity indicated degradation, instead of expected chain extension. Similar behaviour was observed, when photochomical conditions were employed. For the latter purpose, the same polymer (120 mg.) containing 1 ml styrene and 60 mg, dibenzoylperoxide in THF was heated at 60 °C for 45 minutes. The obtained polymer was submitted to fractionation using benzen as a common

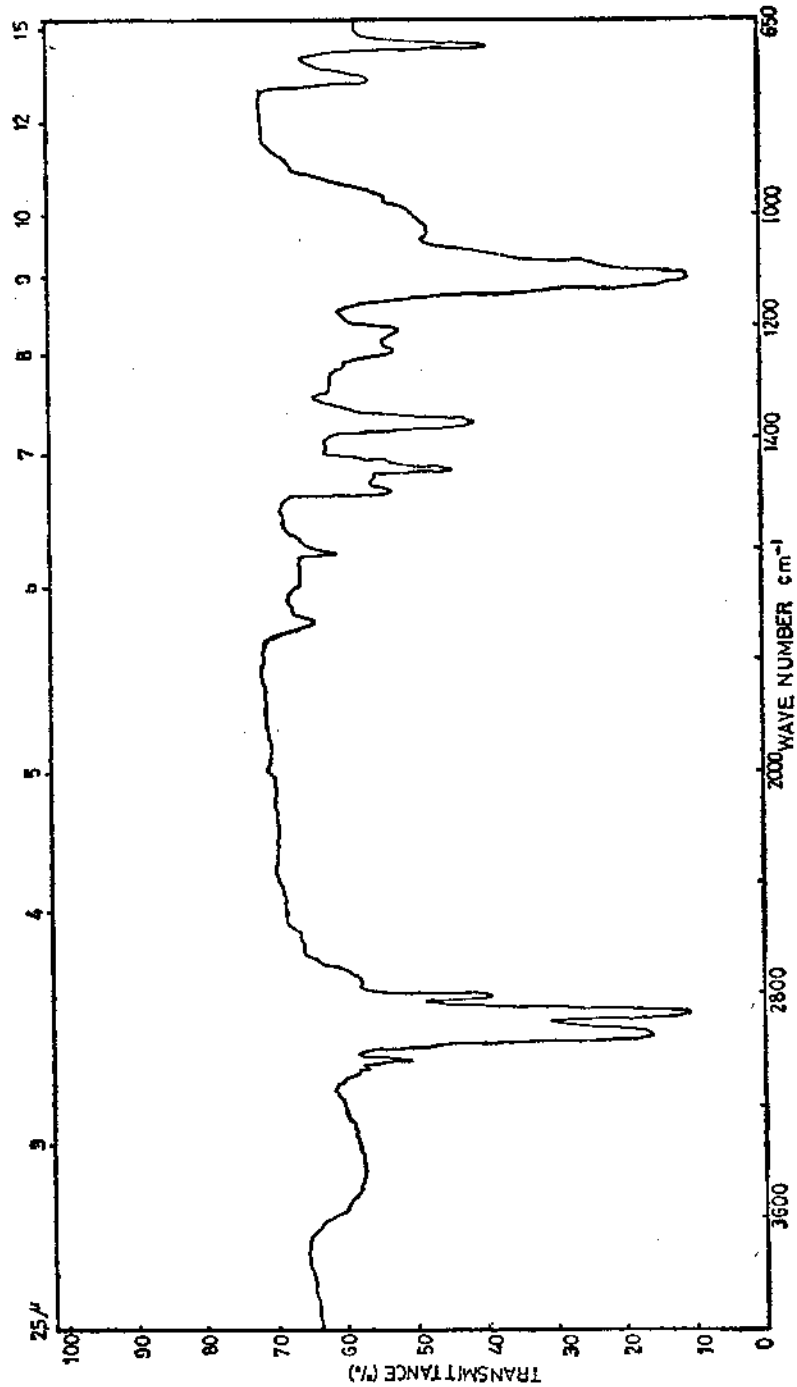


Figure 2. IR spectra of grapht copolymer

solvent and isooctane as a nonsolvent. For the pricipitation of the graft co polymer, it seemed appropriate to use the fractionation value of $\gamma(0,8)$ taken from the data of Franta et. al.[5] who prepared polystyrene-g-poly-THF free of any homopolymers. Infrared spectra of the fractionated co-polymer is shown in Figure 2.

Detailed studies are now in progress together with preparing polyTHF with functional end groups other than acrylate.

REFERENCES

1 - C. H. Bamford, A. Ledwith and Y. Yağcı Polymer, 19, 354 (1978)

2 - G. C. Eastmond and J. Woo IUPAC symp. on Macromolecus U.S.A. (1982)

3 - A. R. Siebert IUPAC symp. on Macromolecules. Aberdeen, (1973)

4 - H. J. Kreb and W. Heitz Macromol. Chm., Rapid Commun. 2, 427 (1981)

5 - E. Franta, L. Reibel and J. Lehmann J. Poly. Sci., Poly symp. 56, 139 (1976)

6 - Y. Yağçı, A. C. Aydoğan and Ü. Tunca Chim., Act. Turc. 10, 121, (1982)

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