(3) Suzuki, T.; Murakami, Y.; Takegami, Y. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 241.
(4) Rathke, M. W. *J. Am. Chem. Soc.* **1970**, *92*, 3222.
(5) Rathke, M. W.; Lindert, A. *J. Am. Chem. Soc.* **1971**, *93*, 2318.
(6) Lochmann, L.; Rodová, M.; Trekoval, J. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 2091.
(7) Riddle, E. H. "Monomeric Acrylic Esters"; Reinhold: New York, 1954.
(8) McCloskey, A. L.; Fonken, G. S.; Kluiber, R. W.; Johnson, W. S. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. 4, p 261.
(9) Lochmann, L.; Lím, D. *J. Organomet. Chem.* **1973**, *50*, 9.
(10) In the case of the ideal triblock copolymer, PMMA block thus obtained could have the molecular weight calculated from M/I.
(11) Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.* **1960**, *44*, 173.
(12) Inoue, Y.; Nishioka, A.; Chûjô, R. *Polym. J.* **1971**, *4*, 535.

Perfluoroalkylene-Linked Polyquinolines and Related Model Compounds

Francesco A. Bottino, Antonino Mamo, and Antonino Recca*

Faculty of Engineering, University of Catania, 95125 Catania, Italy

John P. Droske and John K. Stille*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.
Received August 10, 1981

ABSTRACT: The synthesis of perfluoroalkylene-linked polyquinolines and related model compounds and the effect of the perfluoroalkylene group on the physical and chemical characteristics of these polymers are described. While the glass transition temperatures of all of the perfluoroalkylene polyquinolines were significantly lower than those of the all-aromatic polyquinolines, the thermal stability was lower only with a large incorporation of perfluoroalkylene groups; i.e., 5% perfluoroalkylene copolymers showed thermal stabilities equal to those of the all-aromatic polyquinolines. The solution viscosity decreased with an increasing incorporation of perfluoroalkylene units. Thus, measurement of the dynamic mechanical properties was only possible with 5% copolymers which had sufficiently high solution viscosities to permit casting good films.

Introduction

The Friedlander reaction has been used extensively to afford high molecular weight polyquinolines.[1-4] The polyquinolines show excellent thermal stability,[1-5] but their processability is often quite limited because of the high T_g's and, in some cases, the low solubility exhibited by these polymers. In an effort to increase the processability of these polyquinolines, the incorporation of flexible fluoromethylene groups into the polymer chain has been investigated and is reported herein. Fluoromethylene incorporation into the chain is appropriate for this purpose because it lowers T_g and maintains chemical inertness as well as thermal, thermooxidative, and radiative stability.[6-13]

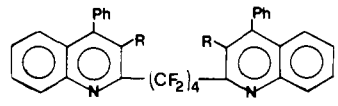
Discussion

Syntheses. The synthesis of 3,3,4,4,5,5,6,6-octafluoro-2,7-octanedione (1) and 1,8-diphenyl-3,3,4,4,5,5,6,6-octafluoro-2,7-octanedione (2) was accomplished by the Grignard reaction of octafluoroadipic acid with methyl- and benzylmagnesium halides (eq 1).

$$HOOC(CF_2)_4COOH + RMgX \rightarrow RCH_2C(O)(CF_2)_4C(O)CH_2R \quad (1)$$

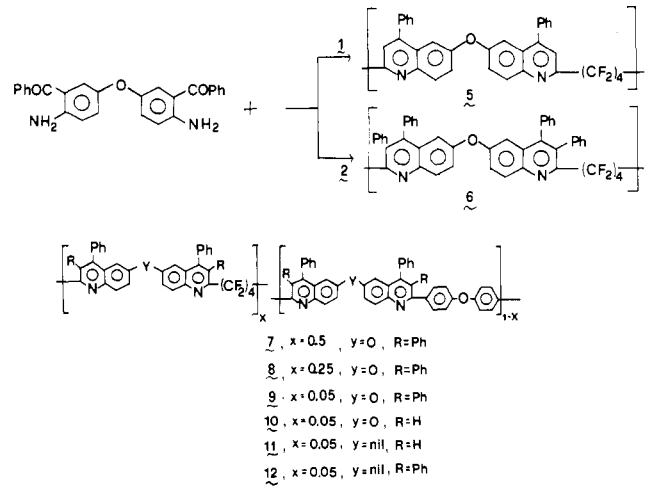
1, R = H
2, R = C_6H_5

The bisquinolines **3** and **4** were prepared by the reaction of 3,3,4,4,5,5,6,6-octafluoro-2,7-octanedione (1) or 1,8-diphenyl-3,3,4,4,5,5,6,6-octafluoro-2,7-octanedione (2) with 2-aminobenzophenone in a chloroform–di-*m*-cresyl phosphate medium.[4] The presence of the parent ions (*m/e*



3, R = H
4, R = Ph

Scheme I



7, x = 0.5, y = O, R = Ph
8, x = 0.25, y = O, R = Ph
9, x = 0.05, y = O, R = Ph
10, x = 0.05, y = O, R = H
11, x = 0.05, y = nil, R = H
12, x = 0.05, y = nil, R = Ph

608 and 760 for **3** and **4**, respectively) in the mass spectrum of both materials was an indication of their stability.

All polymerizations were conducted in *m*-cresol–di-*m*-cresyl phosphate medium.[4] Polymers **5** and **6** were prepared by the reaction of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether with monomers **1** and **2**, respectively, while copolymers **7–9** were obtained from 4,4′-diamino-3,3′-dibenzoyldiphenyl ether with monomer **2** and 4,4′-diphenacetyldiphenyl ether in the appropriate balance (Scheme I). The polymerization of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether with monomer **1** (5%) and 4,4′-diacetyldiphenyl ether (95%) afforded copolymer **10**, and copolymers **11** and **12** were prepared from 3,3′-dibenzoylbenzidine[3] with 4,4′-diacetyl- or -diphenacetyldiphenyl ether and monomers **1** and **2**, respectively, in the appropriate balance.

Phase Transition Temperatures, Thermal Stabilities, and Dynamic Mechanical Properties. Pressed powder samples of the perfluoroalkylene-linked poly-

0024-9297/82/2215-0227$01.25/0

Table I
Properties of Polyquinolines 5–12

polymer	solubility[a]	$[\eta]$,[b] dL/g	T_g(DSC), °C	TGA air[c]	TGA N_2[c]	TGA % weight loss at 800 °C (N_2)
5[d]	$CHCl_3$	0.19 (1.80)	141[f] (266)	370	387	33
6[d]	TCE[e]	0.21 (2.00)	183[f] (305)	372	390	35
7	$CHCl_3$	0.25	199	442	475	31
8	$CHCl_3$	0.28	234	470	480	36
9	$CHCl_3$	0.51	255	545	580	38
10	$CHCl_3$	0.53	225	560	585	12
11	*m*-cresol	0.91	275	540	590	31
12	*m*-cresol	0.85	285	580	603	26

[a] Solubility defined as the ability to dissolve 5% by weight of polymer. [b] Intrinsic viscosity determined in $CHCl_3$ at 25 °C. [c] Onset of weight loss from decomposition. [d] Values in parentheses indicate the viscosities and T_g's of the homopolymers containing only diphenyl ether without the perfluoroalkylene group.[5] [e] *sym*-Tetrachloroethane. [f] Sample annealed at 200 °C for 1 h and then cooled with liquid nitrogen.

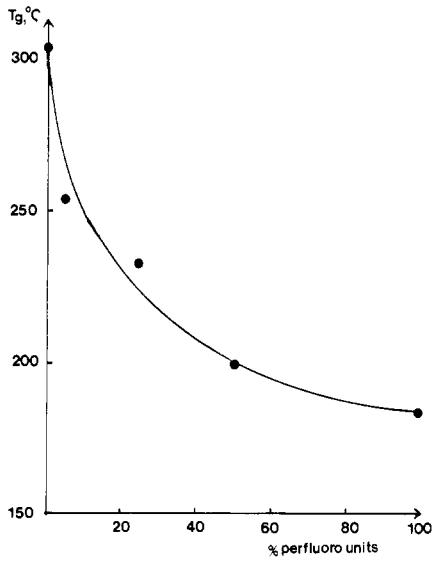


Figure 1. T_g as a function of the perfluoro unit percentage in the chain for polymers **6–9**.

quinolines were analyzed by differential scanning calorimetry (DSC). The T_g's of polyquinolines **5** and **6** were ~120 °C lower than the T_g's of the corresponding polyquinolines containing diphenyl ether instead of the octafluorobutylene groups (Table I and ref 5). Polymers **6–9**, containing different percentages of perfluoroalkylene groups, showed decreasing T_g's with increasing percentage of perfluoroalkylene groups in the chain (Figure 1). Copolymers **9–12** exhibited T_g's that were 30–50 °C lower than the T_g's of the all-aromatic polyquinolines[1-5] without perfluoroalkylene groups even though they contained only 5% incorporation of perfluoroalkylene groups.

Polyquinolines **5** and **6** had good thermal stabilities in both air and nitrogen atmospheres (Table I). Thermogravimetric analysis (TGA) showed initial weight losses occurring at 370 °C in air and 390 °C in nitrogen, whereas the all-aromatic polyquinolines without perfluoroalkylene groups exhibited initial weight losses at ~500 °C.[1] However, copolymers **7–12** showed initial weight losses at temperatures above those of the perfluoroalkylene homopolymers, and copolymers **9–12** (containing octafluorobutylene groups in the chain) showed the same decomposition temperatures as the corresponding all-aromatic polyquinolines lacking the perfluoroalkylene linkage (Table I, ref 1–5).

Table II
Thermomechanical Properties of Polyquinolines 9–12

copolymer	$E'_{25\,°C}$, dyn/cm²	$T_g(E''_{max})$, °C
9	2.2×10^{10}	236
10	2.2×10^{10}	189
11	2.4×10^{10}	259
12	2.3×10^{10}	284

Although elemental analysis of the monomers suggested good purity, the solution viscosities of the fluorine-containing homopolymers **5** and **6** are much lower than those of the all-aromatic polyquinolines, and films cast from a 5% solution and dried under reduced pressure at 140 °C were brittle. This difference in solution viscosity may be due to lower molecular weight but also may be due to the high degree of mobility introduced by the perfluorobutylene groups. In an attempt to circumvent this problem, copolymers **7–9**, containing different percentages of perfluorobutylene groups in the chain, were synthesized. In the case of copolymers **7** and **8**, the solution viscosities were still low and the resulting films were brittle. However, copolymer **9** (containing 5% of the perfluorobutylene units in the chain) had a higher viscosity (Table I) and a good film was cast from chloroform solution. As a result, copolymers **10–12**, all containing 5% of the perfluorobutylene units, were synthesized. Each of these copolymers had a sufficiently high solution viscosity (Table I) to permit casting of good films. The ability to cast a film with copolymer **12** is especially significant because a film could not be cast with the corresponding polyquinoline without the perfluoroalkylene group due to the insolubility of the polymer in all solvents.[3]

The dynamic mechanical properties of copolymers **9–12** were determined (Figure 2, Table II). Young's modulus at room temperature for each of the copolymers was approximately the same as those of the corresponding all-aromatic polyquinolines[1,3-5] without the perfluoroalkylene incorporation (except for copolymer **12**, which does not have reference properties due to the inability to cast a film). The maximum of loss modulus (E''_{max}) paralleled the decrease in T_g as determined by DSC for the perfluoroalkylene-linked polyquinolines compared to the all-aromatic polyquinolines (Table II).

Thus, a small percentage (~5%) of perfluorobutylene groups in the polyquinoline chain is sufficient to lower the T_g significantly (Figure 1, Table I) while maintaining or increasing desirable solution, film, and mechanical properties as well as thermal stability.

Table III
Elemental Analyses of Bisquinolines 3 and 4 and Polyquinolines 5-12

	calcd				found				
sample	% C	% H	% F	% N	% C	% H	% F	% N	% residue
3	67.10	3.29	25.00	4.60	66.34	3.38	24.78	4.47	
4	72.63	3.68	20.00	3.68	71.53	3.72	19.51	3.52	0.39
5	65.60	2.89	24.44	4.50	65.56	3.14	25.59	4.63	2.76
6	71.32	3.38	19.62	3.61	71.14	3.45	18.77	3.84	
7	79.16	3.96	10.03	3.69	77.05	4.02	10.66	3.42	2.65
8	83.18	4.29	5.06	3.72	83.26	4.37	4.97	3.69	
9	86.48	4.55	1.02	3.76	85.97	4.68	0.82	4.10	
10	84.38	4.33	1.28	4.73	83.15	4.45	0.99	4.60	0.66
11	86.73	4.45	1.32	4.86	86.28	4.47	0.82	4.80	0.71
12	88.38	4.65	1.04	3.84	86.97	4.72	0.71	3.74	

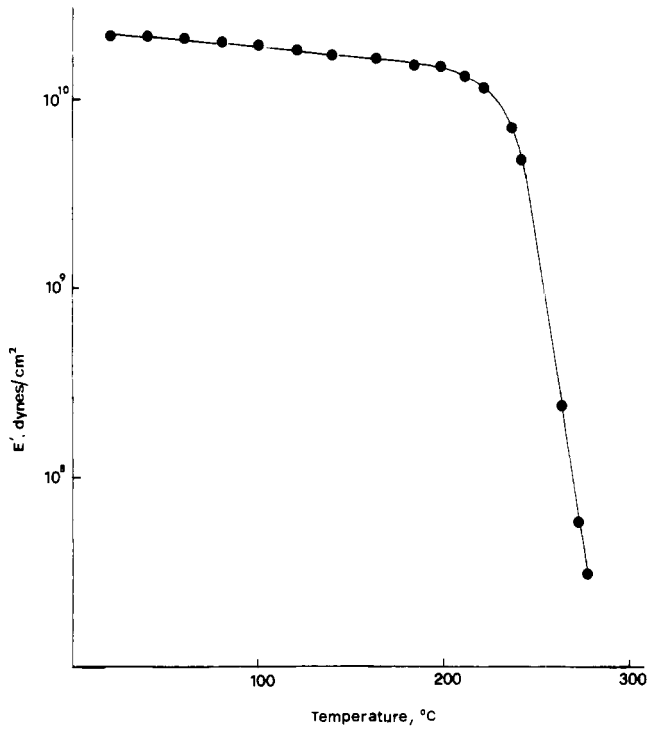


Figure 2. E' vs. temperature for copolymer **9**.

Experimental Section

Octafluoroadipic Acid.[13] The commercial product was dried under reduced pressure (0.15 mmHg) at room temperature for 2 h. The residue was then kept overnight in a desiccator over solid potassium hydroxide to remove the hydrofluoric acid and then it was sublimed at 100 °C and 0.15 mmHg; mp 136–138 °C (lit.[13] mp 134–135 °C).

3,3,4,4,5,5,6,6-Octafluoro-2,7-octanedione (1). In a conventional apparatus fitted with a drying tube, 1.48 g (60.9 mmol) of magnesium was stirred overnight in the presence of a crystal of iodine under a nitrogen atmosphere; 10 mL of anhydrous ether was then added to the flask from the dropping funnel followed by 20 drops of methyl iodide. A solution of 8.88 g (62.6 mmol) of methyl iodide in 20 mL of ether was added dropwise with stirring at a rate that maintained the reflux. The reaction mixture continued to reflux for an additional 10 min. To this solution, a mixture of 3.0 g (10 mmol) of perfluoroadipic acid in 10 mL of ether was added dropwise at a rate that kept the reaction mixture refluxing (20 min). After the addition was complete, the mixture was heated to reflux for an additional 2 h. The mixture was decomposed after cooling in an ice-water bath by the addition of a mixture of concentrated HCl and water. The aqueous layer was separated and extracted with ether, the ether extracts were combined with the original ether layer, and the ether solution was washed with a saturated solution of sodium bicarbonate until neutral and then with water. After drying ($MgSO_4$) the ether solution was evaporated to give a transparent oil. Distillation of the oil [72–75 °C (20 mmHg)] gave 0.75 g (25%) of 1: ^{1}H NMR ($CDCl_3$) δ 2.37 (6 H, s, CH_3); ^{19}F NMR ($CFCl_3$) δ -200.40 (2 F, t, CF_2), -202.10 (2 F, t, CF_2); IR (KBr) 1743 cm^{-1} (ν(C=O)). Anal. Calcd for $C_8H_6F_8O_2$: C, 33.60; H, 2.10; F, 53.11. Found: C, 33.64; H, 2.22; F, 52.53. The residual oil from the distillation solidified in the refrigerator; recrystallization from benzene yielded 0.42 g (13%) of 2,7-dimethyl-3,3,4,4,5,5,6,6-octafluorooctanediol: mp 79–81 °C; ^{1}H NMR δ 1.40 (12 H, s, CH_3). Anal. Calcd for $C_{10}H_{14}F_8O_2$: C, 37.73; H, 4.39; F, 47.77. Found: C, 37.78; H, 4.49; F, 44.93.

1,8-Diphenyl-3,3,4,4,5,5,6,6-octafluoro-2,7-octanedione (2). This compound was prepared following the published procedure;[13] mp 101–102 °C (lit.[13] mp 104–105 °C).

Model Compounds. The synthesis of bisquinoline **3** is given below as a general procedure and was the procedure used for the reaction affording **4**. To a resin flask were added 0.7890 g (4.000 mmol) of 2-aminobenzophenone, 0.8130 g (2.000 mmol) of **1**, 15.5 g of di-*m*-cresyl phosphate, and 5 g of freshly distilled chloroform. The flask was purged with nitrogen, and the solution was stirred for 24 h under a static nitrogen atmosphere at 130 °C. The compound was isolated by precipitating the solution into a stirring solution of 300 mL of ethanol and 30 mL of triethylamine to afford a white precipitate. The product was collected by filtration, air-dried, and dried under reduced pressure at 110 °C for 24 h to give 1.4 g (83% yield) of **3**: mp 228–229 °C; *m/e* 608. The bisquinoline **4** was prepared by the same procedure, starting from compound **2**, to give a 79% yield: mp 255 °C; *m/e* 760. The elemental analyses are reported in Table III.

Polymerizations. The synthesis of polymer **5** is given below as a general procedure for the polymerization reaction and was the method for the synthesis of polymer **6** and the copolymers **7–12**. To a resin flask were added 0.6652 g (1.628 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether, 0.4632 g (1.628 mmol) of monomer **1**, 11 g of di-*m*-cresyl phosphate, and 3 g of freshly distilled *m*-cresol. The flask was purged with nitrogen, and the solution was stirred for 48 h under a static nitrogen atmosphere at 135 °C. The polymer was isolated by precipitating the dark mixture into a stirring solution of 150 mL of ethanol and 30 mL of triethylamine to afford a white precipitate. The polymer was collected by filtration and dissolved in 20 mL of *sym*-tetrachloroethane. This solution was slowly poured into a stirred solution of ethanol/triethylamine, and the resultant precipitate was chopped in a blender and collected by filtration. The polymer was continuously extracted with a solution of ethanol/triethylamine for 24 h, filtered, and dried under reduced pressure at 110 °C for 24 h to afford a cream-colored polymer (see Table III for elemental analysis).

Glass Transitions, Thermogravimetric Analyses, and Dynamic Mechanical Properties. Thermal transitions were measured with a differential scanning calorimetry cell attachment for a DuPont 990 differential thermal analyzer under a 55 mL/min flow of nitrogen and at a heating rate of 10 °C/min, with air as reference. The DuPont 951 thermogravimetric analyzer attachment was used at a heating rate of 5 °C/min under circulating air or nitrogen atmospheres. The dynamic mechanical properties were determined at a heating rate of 5 °C/min and an applied frequency of 35 Hz using the Rheovibron (Toyo Baldwin Co., Ltd., Model DDV-II-C).

Acknowledgment. We gratefully acknowledge support of this research by NATO and the U.S. Army Research Office, Durham, N.C. We also thank Dr. P. D. Sybert for

the sample of 3,3′-dibenzoylbenzidine, and J.P.D. is thankful to the Phillips Petroleum Foundation for a fellowship.

References and Notes

(1) For a review, see: Stille, J. K. *Macromolecules* **1981**, *14*, 870.
(2) Stille, J. K.; Harris, R. M.; Padaki, S. M. *Macromolecules* **1981**, *14*, 486.
(3) Sybert, P. D.; Beever, W. H.; Stille, J. K. *Macromolecules* **1981**, *14*, 493.
(4) Beever, W. H.; Stille, J. K. *J. Polym. Sci., Polym. Symp.* **1978**, *No. 65*, 41.
(5) Wrasidlo, W.; Norris, S. O.; Wolfe, J. F.; Katto, J. F.; Stille, J. K. *Macromolecules* **1976**, *9*, 512.
(6) Burton, C. D.; Madison, N. C. U.S. Patent 3 560 438, 1971.
(7) Evers, R. C. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1974**, *15*, 685.
(8) Hergenrother, P. M. U.S. Patent 3 773 412, 1973.
(9) Hergenrother, P. M.; Rafter, R. T.; Harrison, E. S. *J. Macromol. Sci., Chem.* **1975**, *A9*, 1289.
(10) Dorfman, E.; Emerson, W. E.; Carr, R. L. K.; Bean, C. T. *Rubber Chem. Technol.* **1966**, *39* (4), Pt 2, 1175.
(11) Dorfman, E.; Emerson, W. E.; Gruber, R. J.; Lemper, A. A.; Rushston, B. M.; Graham, T. L. *Angew. Makromol. Chem.* **1971**, *16/17*, 75.
(12) Hergenrother, P. M. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1978**, *19*, 40.
(13) Hergenrother, P. M.; Hudlicky, H. *J. Fluorine Chem.* **1978**, *12*, 439.

New Binary Lanthanide Catalysts for Stereospecific Diene Polymerization

Ji-Hua Yang,*[1] M. Tsutsui,[2] Zonghan Chen,[3] and David E. Bergbreiter*

Department of Chemistry, Texas A & M University, College Station, Texas 77843.
Received August 13, 1981

ABSTRACT: New binary lanthanide catalysts composed of tetrahydrofuran adducts of lanthanide chlorides and triethylaluminum in hydrocarbon solvents which stereospecifically polymerize butadiene and isoprene are described. For example, the catalyst composed of $NdCl_3$·2THF with Et_3Al can be used to form both polybutadiene and polyisoprene with 97% and 95% cis-1,4 units, respectively, with good activity. The organometallic intermediates in these polymerizations have been shown to be reactive enough to be successfully quenched with carbon dioxide to form carboxylic acids.

The discovery of lanthanide and actinide catalysts for stereospecific polymerization of dienes has led to the development of Ziegler–Natta catalysts from f-orbital elements and confirmed the belief that the expansive coordination as well as the f-symmetry valence orbitals of the lanthanides and actinides can display useful catalytic properties related to those of d-transition metals. In stereospecific polymerization of dienes with Ziegler–Natta type catalysts, only lanthanide catalysts and uranium catalysts are known to give high *cis*-1,4-polybutadiene, high *cis*-1,4-polyisoprene, and their copolymer containing both monomer units with high cis-1,4 geometry.[4,5] Consequently, further research into and development of lanthanide catalysts for diene polymerization has aroused great interest.

Shen, Ouyang, et al.[6] first used a lanthanide catalyst which was a binary system composed of $LnCl_3$ (Ln = Y, La, Ce, Pr, Nd, Sm, Gd, Er, and Yb) and AlR_3 (R = Et, *i*-Bu) in polymerization of butadiene. The resulting catalysts' stereospecificity was high, but their catalytic activity was rather low. Throckmorton modified the catalyst system from binary to a ternary system (cerium octanoate–AlR_3–halide) and found polymerization activity was increased.[7] However, a drawback of this system is the requirement that the Ce-containing residues must be completely removed from the resulting polymers because cerium ion can promote rubber oxidation. Since 1970, Chinese chemists have developed a new "family" of lanthanide catalysts based on neodymium compounds or a mixture of neodymium and praseodymium compounds. These elements were found to be the most active elements in the series of lanthanides. Some three-component systems which were first developed include lanthanide naphthenate, lanthanide carboxylates, or lanthanide phosphates together with AlR_3 and added halide.[8] These catalysts are used for butadiene polymerization, for isoprene polymerization, and for butadiene and isoprene copolymerization. Subsequently, it was found that the addition of suitable amounts of alcohol to the original system ($LnCl_3$–AlR_3) led to greatly enhanced activities without any decrease in stereospecificity.[9] Further investigation revealed that the lanthanide halide first reacts with the added alcohol to form an alcoholate which then reacts with AlR_3 to form an active catalyst. Thus, a new efficient binary system of $LnCl_3$·3ROH–AlR_3 has been established. Other binary catalysts such as $NdCl_3$·3P_{350} (P_{350} = $((CH_3(CH_2)_5CH(CH_3)O)_2POCH_3)$[8] or $NdCl_3$·3TBP (TBP = triisobutyl phosphate)[10] with AlR_3 were also developed. Recently, a few USSR patents concerning polymerization of dienes using $LnCl_3$·Me_2SO (Me_2SO = dimethyl sulfoxide) or $LnCl_3$·*n*HMPA (HMPA = hexamethylphosphoramide) with AlR_3 have been cited.[11]

Here we report that a new binary system composed of $NdCl_3$·2THF with $AlEt_3$ also is an efficient catalyst for diene polymerization in hydrocarbon solvents. Since THF is a very useful solvent for many organometallic syntheses and since it does not react with AlR_3 other than to form a Lewis acid–base complex, this catalyst system will be an attractive system for study of these lanthanide polymerization catalysts, their reactions, and possible intermediates in the polymerization process.[12] In addition, we have shown the reactive nature of the organometallic intermediates in these polymerizations by trapping polymeric intermediates with carbon dioxide.[13]

Results and Discussion

THF is a very useful solvent for many organometallic syntheses in part because of its aprotic nature and its ability to complex with metal salts. It was known that anhydrous lanthanide chloride salts also readily form

0024-9297/82/2215-0230$01.25/0