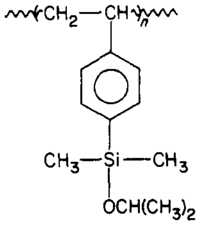
polymers still had narrow molecular weight distributions and that broadening of the distribution was not observed in all cases. In practice there is no problem concerning the influence of such reactions on the polymerization of **4**. Since the anionic polymerization of **4** appears to occur almost instantaneously at −78 °C and the decomposition reactions are completely suppressed even after 30 min, as shown in Table III and IV.

Some Properties of Poly[(4-vinylphenyl)dimethyl-2-propoxysilane] (6). Polymer **6** is a white solid and soluble in benzene, toluene, *n*-hexane, cyclohexane, tetrahydrofuran, 1,4-dioxane, diethyl ether, carbon tetrachloride, chloroform, dichloromethane, acetone, methyl ethyl ketone, methyl isobutyl ketone, *n*-butyl alcohol, and *N*,*N*-dimethylformamide but insoluble in water, methanol, and ethanol. The solubility of **6** resembles very closely that of polystyrene, except for *n*-hexane in which the latter is insoluble.



6

6 can be cast from THF solutions to give a transparent, colorless, and brittle film.

Polymer **6** has a glass transition temperature of 180 °C, which was determined by differential scanning calorimetry. This value is about 80 °C higher than that of polystyrene, probably due to the steric bulkiness of **6** arising from the presence of the dimethyl-2-propoxysilyl substituent.

As expected, **6** is readily cross-linked by hydrolysis of the alkoxysilyl groups and subsequent condensation between the two resulting silanol groups. For example, when **6** was dissolved in THF and the solution treated at room temperature with a little aqueous 6 N hydrochloric acid, irreversible precipitation of the polymer occurred. Similarly, it is possible to cross-link **6** in film form by treatment with gaseous hydrochloric acid. The resulting polymers are highly cross-linked materials and hence insoluble in organic solvents and water. Applications of **6** are currently under study.

Registry No. **3**, 17983-64-1; **3** (homopolymer), 98542-13-3; **4**, 58556-56-2; **4** (homopolymer), 98542-14-4; **5**·Li, 98611-50-8; **5**·K, 98611-49-5; 2-propoxydimethylchlorosilane, 1825-71-4; 4-vinylphenyl chloride, 1073-67-2; dimethyldichlorosilane, 75-78-5; 2-propanol, 67-63-0; dimethoxydimethylsilane, 1112-39-6.

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Reactive Site and Mechanism of Graft Copolymerization onto Poly(ether urethane) with Ceric Ion as Initiator

X. D. Feng,*[†] Y. H. Sun, and K. Y. Qiu

Department of Chemistry, Peking University, Beijing, China. *Received October 10, 1984*

ABSTRACT: The reaction mechanism of graft copolymerization of acrylamide onto poly(ether urethane) (PEU) initiated by ceric ion was investigated. A series of organic compounds were used as the model compounds for the functional groups and different segments of PEU, and the graft copolymerization onto PEUs having different compositions was carried out. It was found that the phenyl carbamate group ($1,4\text{-}C_6H_4NHCOO\text{–}$) in the hard segment is highly reactive. The reaction mechanism was then proposed for the first time to involve the complex formation between a ceric ion and a carbamate group as the first step, followed by its decomposition into free radical on the N atom as the main site of grafting. Therefore, the main reactive site of graft copolymerization initiated by ceric ion would take place predominately at the hard segments of PEU.

Introduction

Although successful graft copolymerizations of acrylamide onto poly(ether urethane) (PEU) films[1,2] were performed by using ceric salt as an initiator, the reaction mechanism as well as the grafting site of initiation were never reported. We used a series of organic compounds as the models for the functional groups and the different segments of PEU and compared their reaction activities in the rate of vinyl polymerization. Then we examined the influence of the hard and soft segments of PEU on the graft reaction and also the relationship between the PEU structures and the grafting reactivities from which the reactive site and the reaction mechanism of graft copolymerization is then proposed.

Experimental Section

Materials. Acrylamide (AAM) was recrystallized from acetone three times, mp 84 °C. Ammonium ceric nitrate and solvents were used as reagent-grade chemicals. *N*-Methylacetanilide was prepared by the reaction of acetic anhydride with *N*-methylaniline. *p*-Substituted acetanilides were synthesized from acetic anhydride and corresponding para-substituted anilines. Poly(tetramethylene ether) glycol (PTMG) was obtained from Du Pont. Poly(ether

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[†] Formerly known as S. T. Voong.

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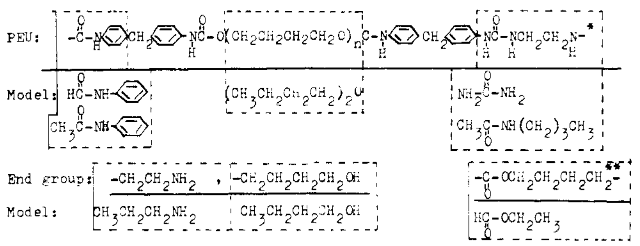


Figure 1. Model compounds of different functional groups of PEU: (*) diamine extended; (**) diol extended.

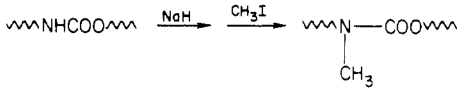
urethane) (PEU) was synthesized from PTMG, 4,4′-methylenediphenyl diisocyanate, and butanediol by a melting-solution two-step process. Model compounds of PEU segments PU-II, PU-III, and U-IV were prepared by the methods described previously.[3,4]

Determination of AAM Polymerization Rate Initiated by Ceric Salt and Model Compound. The AAM aqueous solution containing the model compound was deaerated by nitrogen gas, and then ceric salt solution was added. The solution was poured quickly into a dilatometer and put in a thermostatic water bath. The volume change was recorded.

The hard segment models PU-II, PU-III, and U-IV were crushed into tiny powder (their structures are given in the next section) and distributed in AAM solution. The polymerization rate was measured by the same method as described above.

Polyether wax was placed in a dilatometer bottle and warmed into liquid. The bottle was rotated so as to coat the bottle wall with PTMG as evenly as possible. After polyether was solidified by cooling, the bottle was used to measure the polymerization rate (R_p) of AAM.

Preparation of Methylated PEU. Methylated PEU was prepared according to ref 5.



$$\sim\sim NHCOO\sim\sim \xrightarrow{NaH} \xrightarrow{CH_3I} \sim\sim \underset{CH_3}{\underset{|}{N}}—COO\sim\sim$$

Graft Copolymerization onto PEU Film. A piece of PEU film with known weight and dimensions was put into an Erlenmeyer flask containing AAM aqueous solution, immersing for 15 min and bubbling with nitrogen gas for another 15 min. Then the freshly prepared ceric salt solution was added. Under the protection of nitrogen gas, the graft reaction was carried out at room temperature by using an electromagnetic stirrer. After the reaction was run for a certain period, the film was extracted with three 300-mL portions of boiling water for 72 h.

Results and Discussion

Although ceric salt can react with AAM monomer, producing monomeric radicals, to initiate polymerization,[6] the graft copolymerization of AAM onto the PEU backbone always took place before homopolymerization.[1,2] From the mechanistic point of view, this fact indicates that the graft reaction onto PEU film was not initiated through the chain transfer of macroradical from monomer in solution and the reactivity of ceric ion with PEU is greater than with the AAM monomer. Hence there must be some reactive functional group in the PEU backbone onto which the graft copolymerization could easily take place. It is our chief object in this paper to identify such reactive sites and then propose the reaction mechanism of graft copolymerization in some detail.

AAM Polymerization Initiated by Ceric Salt in the Presence of Model Compounds of Functional Groups in PEU. The structure of PEU is rather complicated; it contains several different functional groups, including carbamate group, ether linkage, and urea linkage. It is also possible that PEU has some hydroxyl end groups or amino end groups. We chose the model compounds in Figure 1 to observe the interactions of these groups with the ceric ion.

Table I
Polymerization of AAM[a]

model compound	rate of polymerization (R_p), × 10^5 mol/(L·s)	rel rate (R_r)	mol wt × 10^5 [b]	overall act energy (E_a), kcal/mol, 17-35 °C[c]
$CH_3CONHC_6H_5$	13.9	2.61	9.76	4.82
$HCONHC_6H_5$	13.0	2.44	9.33	4.88
n-BuOH	6.45	1.21	5.87	13.3
n-$PrNH_2$	6.29	1.18	6.04	13.5
$HCOOCH_2CH_3$	5.95	1.12	8.70	
CH_3CONH-n-Bu	5.90	1.10	5.40	
NH_2CONH_2	5.48	1.03		
$(n\text{-}Bu)_2O$	5.39	1.01	5.96	
0	5.32	1.00	5.94	14.2

[a] [AAM] = 2.5 M, [Ce^{4+}] = [model compound] = 5.0 × 10^{-3} M, 25.0 °C, aqueous solution. [b] Determined by viscometry. [c] Dilatometer method.

Table II
Polymerization of AAM[a]

amide	amide concn mol/L	rate of polymerization (R_p), × 10^5 mol/L	rel rate (R_r)
$CH_3CONHC_6H_5$	5.0 × 10^{-3}	13.9	2.61
HCO-NHC_6H_5	5.0 × 10^{-3}	13.0	2.44
CH_3CONH-c-C_6H_{11}	5.0 × 10^{-3}	5.55	1.04
$HCONH_2$	5.0 × 10^{-3}	5.26	0.989
CH_3CONH-n-Bu	5.0 × 10^{-3}	5.90	1.11
$HCONMe_2$	5.0 × 10^{-3}	5.39	1.01
$HCONMe_2$	4.0 × 10^{-2}	5.89	1.11
	0	5.32	1.00

[a] [AAM] = 2.5 M, [Ce^{4+}] = 5.0 × 10^{-3} M, 25.0 °C, aqueous solution.

Table III
^1H NMR Data of FA and AA in $CDCl_3$

compound	δ_{NH}, ppm	δ_{CHO}, ppm	δ_{COCH_3}, ppm
FA	7.65	8.34, 8.63	
FA + Ce^{4+}	7.83	8.45, 8.74	
AA	8.70		2.10
AA + Ce^{4+}	8.74		2.12

From Table I, it was found that in the presence of model compounds such as ethyl formate, N-butylacetamide, n-butyl ether or urea the rates of AAM polymerizations were enhanced slightly. n-Butyl alcohol and n-propylamine exhibited somewhat higher reactivities. However, the overall activation energies (E_a) of AAM polymerization initiated by Ce^{4+}–n-butyl alcohol or Ce^{4+}–n-propylamine decreased very little as compared with that initiated by Ce^{4+} alone. So the initiation reactions of the end groups of PEU with the ceric ion seemed not to be important. It is worthy of note that acetanilide (AA) and formanilide (FA) which act as the model compounds of the carbamate group displayed remarkable enhancing effects on the rate of polymerization. In addition, the corresponding E_a values in the presence of AA or FA were only 4.82 or 4.88 kcal/mol, respectively, which clearly indicated the formation of an effective redox initiation system between the anilide and the ceric ion. This has not been reported in the literature. Our further studies showed that the presence of the benzene ring such as in the anilide was most critical because the alkylated amides with the -CONHR structure were no longer active toward AAM polymerization (Table II).

The ^1H NMR data concerning the interaction between anilide and ceric ion are given in Table III. The chemical shifts of FA and AA protons all migrated to the lower field,

Table IV
Polymerization of AAM[a]

anilide	rate of polymerization (R_p) × 10^4 mol/L·s ([HNO_3] = 0)	rel rate (R_r)	rate of polymerization (R_p) × 10^4 mol/L·s ([HNO_3] = 0.025 M)	rel rate (R_r)
$CH_3CONHC_6H_4$-*p*-CH_3	5.83	1.92	2.01	4.57
$CH_3CONHC_6H_5$	4.83	1.59	1.11	2.52
$CH_3CONHC_6H_4$-*p*-Cl	4.22	1.39	0.84	1.91
$CH_3CON(CH_3)C_6H_5$	3.83	1.26	0.53	1.20
	3.04	1.00	0.44	1.00
$CH_3CONHC_6H_4$-*p*-NO_2	2.89	0.95	0.53	1.20

[a] [AAM] = 2.0 M, [Ce^{4+}] = [anilide] = 5.0 × 10^{-3} M, 20.0 °C, polymerized in water–formamide mixed solution (1:2.5 v/v).

showing the formation of complexes between anilides and ceric salt. In addition, the solubility of ceric salt in chloroform was obviously increased in the presence of FA or AA, which served as further evidence for the formation of an anilide–Ce^{4+} complex. When DPPH was added to this solution, the purplish-red color of DPPH disappeared immediately, which indicated that a radical intermediate was involved in the reaction.

In order to get more detailed information about the reaction mechanism of anilide with ceric ion, the AAM polymerizations in the presence of AA derivatives were carried out (Table IV). The structural effect of AA derivatives on the rate of AAM polymerization was determined as *p*-methyl-AA > AA > *p*-chloro-AA > *N*-methyl-AA > *p*-nitro-AA; i.e., an electron-donating group on the benzene ring would enhance the polymerization rate, while an electron-withdrawing group would decrease it. The increase of electron density on the carbonyl group by an electron-donating group on the benzene ring favored the coordination with ceric ion. Therefore, the rate of complex formation seemed to play an important role in the reaction. In addition, the function of the H atom on the nitrogen atom of anilide in the rate of polymerization is also noticeable. When the H atom was replaced by a methyl group such as in *N*-Me-AA, the rate of polymerization decreased sharply. On the basis of the above facts, we propose the reaction mechanism of ceric salt with anilide as follows:

$$Ce^{4+} + H_2O \longrightarrow Ce(OH)^{3+} + H^+$$

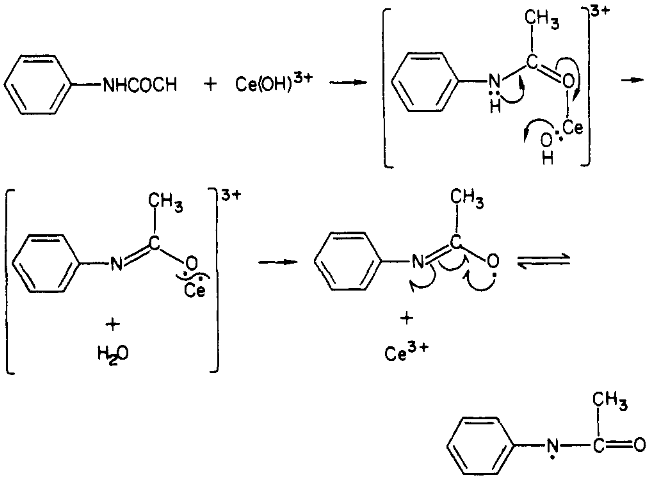
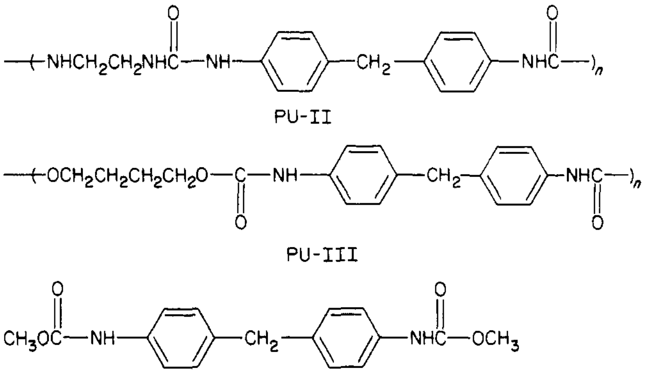


Chart I
Hard-Segment Models



Soft-Segment Model

$$HO\text{—}(CH_2CH_2CH_2CH_2O)_n\text{—}H$$

PTMG

Table V
AAM Polymerization in Heterogeneous System[a]

model	rate of polymerization (R_p), × 10^5 mol/L·s	rel rate (R_r)	wt increase, %
PU-III	10.69	2.01	23.0
PU-III	8.90	1.67	19.8
U-IV	10.32	1.94	
0	5.32	1.00	

[a] [AAM] = 2.5 M, Ce^{4+}] = 5.0 × 10^{-3} M, [model compound] = 50 mg/10 mL, 25.0 °C; the model powder was dispersed in AAM aqueous solution.

AAM Polymerization in the Presence of Some Models of PEU Segments. Several model compounds of the hard and soft segments in PEU were used (see Chart I).

Model Compounds of Hard Segment. In the presence of PU-II, PU-III, or U-IV, the R_p of AAM increased (Table V) as expected from the R_p values initiated by the Ce^{4+}–anilide system.

The weights of PU-II and PU-III separated from reaction mixture were increased due to the occurrence of graft copolymerization of AAM onto them. This was verified by IR spectra, which confirmed that the phenyl carbamate group in the hard segment of PEU was responsible for initiation of graft copolymerization.

Model Compounds of Soft Segment. Ohtsuka[7] et al. have reported that poly(ethylene oxide) could couple with Ce^{4+}, forming a redox system to initiate polymerization. But in our research work we discovered that carefully purified glycol derivatives and poly(ethylene oxide) were very inert toward ceric salt unless they were used directly without purification. Pure PTMG behaved similarly (Table VI). It was seen that PTMG stored over a period of years even at room temperature revealed outstanding reactivity toward polymerization. From a series of structural analyses of PTMG such as IR and NMR spectra (Figures 2 and 3), we found that the stored samples always contain some –OOH, –CHO, and formate groups, among which the aldehyde proved to be the most effective for initiating polymerization.[3] To confirm its oxidation the pure PTMG was subjected to air oxidation at 55 °C. The oxidized PTMG with a –CHO group accelerates the polymerization considerably (Table VI). So we propose that the more active site to react with ceric ion is the –CHO group rather than the polyether linkage. As a result, the

Table VI
R_p Values of AAM in the Presence of PTMG[a]

PTMG	store time, year	rate of polymerization (R_p), × 10^5 mol/L·s	rel rate (R_r)
PTMG-1100[b]	3	12.1	3.09
PTMG-1100	2	8.15	2.09
PTMG-1000	1/2	4.13	1.06
PTMG-2000	1/2	4.06	1.04
		3.90	1.00
PTMG-1000 (after oxidation)	1/2	35.2	9.03

[a] [AAM] = 2.0 M, [Ce^{4+}] = 5.0 × 10^{-3} M, 20.0 °C. [b] The numeric value approximates the molecular weight of PTMG.

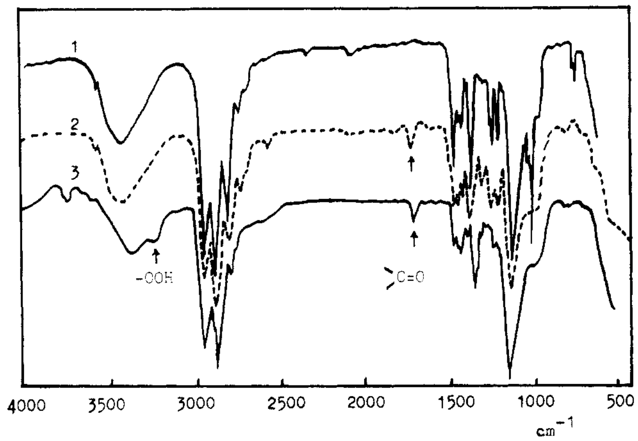


Figure 2. IR spectra of PTMG: (1) PTMG-1000 (new product); (2) PTMG-1000 (new product, after air oxidation at 55 °C); (3) PTMG-1100 (stored for 3 years). The arrows indicate the new bands of PTMG after oxidation or storage for a certain period.

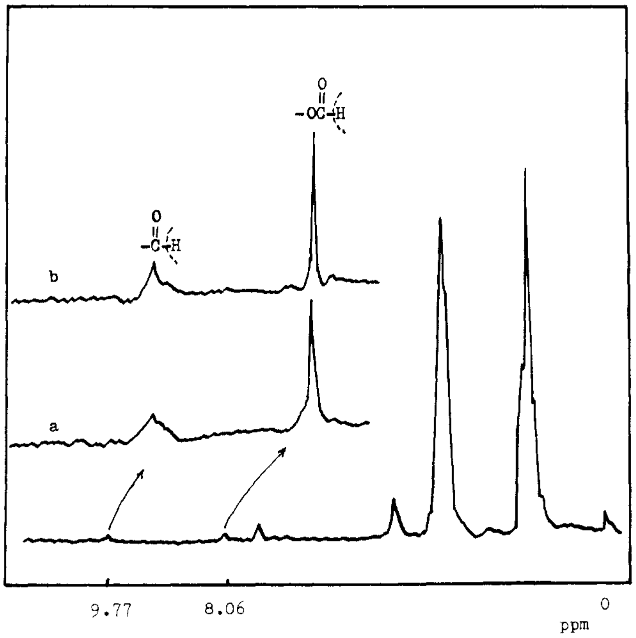


Figure 3. NMR spectra of PTMG-1100 stored for 3 years: (a) curve was accumulated 120 times; (b) curve was accumulated 120 times in the presence of D_2O. The arrows indicate the accumulated peaks at 8.06 and 9.77 ppm, respectively.

pure polyether segment would not act as the grafting site.

Graft Copolymerization of AAM onto PEU. We compared the graft reactivities of different types of multiphase polymers such as PEU and poly(ether ester) (Hytrel) with similar polyether contents. The grafting yield of PEU powder was found to be 4.5 times as high as that of Hytrel powder (Table VII). Obviously, the hard segment of PEU but not the hard segment of poly(ether ester) played an improtant role in grafting. Furthermore, when the hydrogen atom on nitrogen in PEU was substituted by a methyl group, the grafted amount of PAAM decreased sharply from 49.4 mg/cm² to 0.94 mg/cm² (Table VIII). This shows clearly that the hydrogen atom of the phenyl carbamate group in the hard segment of PEU behaves as the main reactive site for graft polymerization. According to the above results and kinetic studies, we propose the reaction mechanism of graft copolymerization as

Table VII
Graft Copolymerization on Polymer Powder[a]

polymer	polyether, %	grafting, %
poly(ether-ester)	42	22.2
PEU	46	99.6

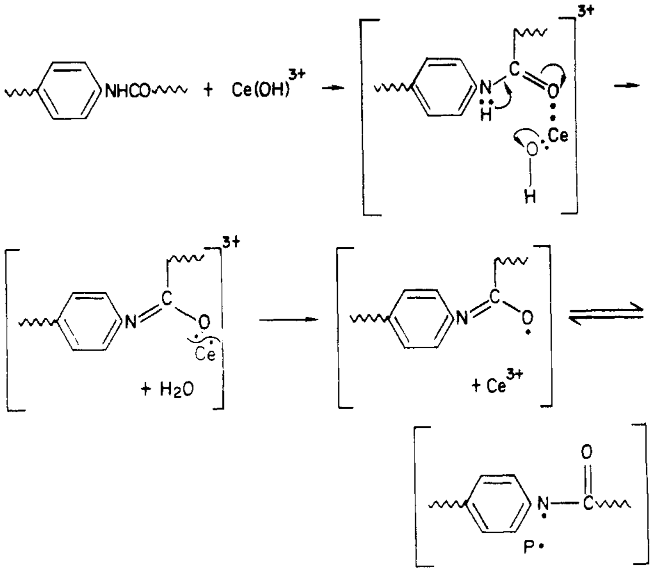
[a] [AAM] = 2.0 M, [Ce^{4+}] = 5.0 × 10^{-3} M, room temperature, 2 h.

Table VIII
Graft Copolymerization on PEU Film[a]

PEU	grafting amount, mg/cm
S-018[b]	49.4
N-methylated S-018	0.94
S-014[b]	4.69
N-methylated S-014	0

[a] [AAM] = 2.0 M, [Ce^{4+}] = 5.0 × 10^{-3} M, room temperature, 1.5 h. [b] PEU code.

$$Ce^{4+} + H_2O \rightarrow Ce(OH)^{3+} + H^+$$



$$P\cdot + M \xrightarrow{K_i} PM\cdot$$
$$PM\cdot + M \xrightarrow{K_p} PMn\cdot$$

Registry No. PU-II, 35744-45-7; PU-III, 25805-16-7; (PU-III)·(PTMG) (copolymer), 9018-04-6; U-IV, 7450-63-7; AAM, 79-06-1; PTMG, 25190-06-1; $HCONHC_6H_5$, 103-70-8; $PrNH_2$, 107-10-8; $HCOOCH_2CH_3$, 109-94-4; $CH_3CONHBu$, 1119-49-9; NH_2CONH_2, 57-13-6; $(Bu)_2O$, 142-96-1; O_2, 7782-44-7; CH_3CONH-c-C_6H_{11}, 1124-53-4; $HCONMe_2$, 68-12-2; $CH_3CONHC_6H_4$-*p*-Cl, 539-03-7; $CH_3CON(CH_3)C_6H_5$, 579-10-2; $CH_3CONHC_6H_4$-*p*-NO_2, 104-04-1; $CH_3CONHC_6H_5$, 103-84-4; *p*-$CH_3C_6H_4NHCOCH_3$, 103-89-9; ammonium ceric nitrate, 16774-21-3; Hytrel, 37282-12-5.

Macromolecules **1985**, *18*, 2109–2113

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Effect of Organometallic Cocatalysts on the Polymerization of 1-Phenyl-1-propyne by $TaCl_5$ and $NbCl_5$[1]

Toshio Masuda,* Akihiro Niki, Eiji Isobe, and Toshinobu Higashimura*

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan.

Received March 25, 1985

ABSTRACT: In the polymerization of 1-phenyl-1-propyne by $TaCl_5$, the polymer formed underwent degradation after all the monomer had been consumed. In contrast, no polymer degradation occurred when suitable organometallics (e.g., tetra-*n*-butyltin, triethylsilane, and triphenylbismuth) were added as cocatalysts at 1:1 ratio to $TaCl_5$. Consequently, polymers with weight-average molecular weights ($\bar{M}_w$) exceeding 1×10^6 could be obtained. Further, use of cocatalysts considerably accelerated the polymerization. Thus a facile method for synthesizing high-molecular-weight poly(1-phenyl-1-propyne) has been established. Polymer degradation was observed also in the polymerization of 1-phenyl-1-propyne by $NbCl_5$, and it was restrained by use of cocatalysts resulting in the formation of polymers with $\bar{M}_w$ around 3×10^5.

1-Phenyl-1-propyne polymerizes in the presence of group 6 transition-metal catalysts, that is, $Mo(CO)_3$·toluene[3] and 1:1 WCl_6–Ph_4Sn[4,5] (see eq 1). However, the molecular weights of the products are no more than several thousand; thus they are so-called oligomers.

$$CH_3C{\equiv}CC_6H_5 \xrightarrow{\text{catalyst}} \left[\underset{CH_3}{C} = \underset{C_6H_5}{C} \right]_n \qquad (1)$$

Niobium (Nb) and tantalum (Ta) are group 5 transition metals and are located immediately to the left of molybdenum and tungsten, respectively, in the periodic table. It has been reported that organo–Nb(III) and –Ta(III) binuclear complexes, $M_2Cl_6(SC_4H_8)_3$ (M = Nb, Ta), polymerize 1-phenyl-1-propyne to high polymers.[6] These complexes are, however, rather difficult to prepare and unstable to air.

The pentachlorides of Nb and Ta induce 1-phenyl-1-propyne to polymerize, and the maximum weight-average molecular weight ($\bar{M}_w$) of the polymer reaches ca. 6×10^5.[2,7] However, this polymerization system had the problem that polymer degradation occurs after all the monomer has reacted, resulting in the complete conversion to oligomers.[2] Thus there was no easy method for preparing high-molecular-weight poly(1-phenyl-1-propyne).

This paper reports on cocatalyst effects of the polymerization of 1-phenyl-1-propyne by $TaCl_5$ and $NbCl_5$. Various organometallics were examined as cocatalysts; they are expected to function as weak reducing agents and as ligands on the active species. Consequently, it was found that they not only accelerate polymerization but also effectively inhibit polymer degradation. Thus a facile method has been established for synthesizing poly(1-phenyl-1-propyne) with $\bar{M}_w$ exceeding one million.

Experimental Section

Materials. 1-Phenyl-1-propyne was purchased from Farchan Labs. and distilled twice at reduced pressure from calcium hydride before use. $NbCl_5$ and $TaCl_5$ were purchased from Alfa, Morton Thiokol, Inc., and used without further purification. Organometallics as cocatalysts were commercially obtained and usually employed without further purification. Polymerization solvents were purified by standard methods, care being taken to remove moisture as completely as possible.

Polymerization. Polymerizations were carried out under dry nitrogen. A typical procedure is as follows (cf. Table I, third row): A monomer solution was prepared by adding 1-phenyl-1-propyne (1.39 g, 1.50 mL, 12.0 mmol) and bromobenzene (0.40 mL, as internal standard for gas chromatography (GC)) to toluene (4.10 mL). A catalyst solution was prepared by mixing $TaCl_5$ (71.6 mg, 0.20 mmol) and tetra-*n*-butyltin (*n*-Bu_4Sn; 69.4 mg, 0.20 mmol) in toluene (5.0 mL) and aged by keeping at 80 °C for 15 min. Then 5 mL of the monomer solution (the residual monomer solution was used for GC) was added to the catalyst solution at 80 °C. After 24 h, the reaction was terminated by adding a mixture of toluene (5 mL) and methanol (0.5 mL). Conversion was determined by measuring the initial and final monomer concentrations through GC (silicone DC 1 m, 140 °C); 100%. The polymerization solution was diluted with toluene (100 mL) and poured into acetone (1 L); methanol, which is often used as a polymer precipitant, was not used because cyclotrimers of 1-phenyl-1-propyne (byproducts) also precipitated in methanol. The polymer was filtered off, washed with acetone, and dried to a constant weight under vacuum. The polymer yield was determined by gravimetry; 76%.

Molecular Weight Measurement. Number-average molecular weights ($\bar{M}_n$) and $\bar{M}_w$ were evaluated by gel permeation chromatography (GPC) using a Jasco Triroter high-performance liquid chromatograph (Shodex A802, A804, A806 polystyrene gel columns, eluent $CHCl_3$, polystyrene calibration). It is known[2] that the $\bar{M}_w$ of poly(1-phenyl-1-propyne) tentatively obtained by GPC on the basis of polystyrene calibration is ca. 1.5 times as large as the "true" $\bar{M}_w$ determined by the light-scattering method.

Results

Polymerization by $TaCl_5$. Figure 1 shows time changes of conversion and polymer $\bar{M}_w$ in the polymerization of 1-phenyl-1-propyne by $TaCl_5$ alone.[8] Under the conditions shown in Figure 1, conversion reached 100% at about 6 h. The $\bar{M}_w$ of polymer increased with increasing conversion to become ca. 6×10^5 at 100% conversion.[9] However, when the reaction system was allowed to stand for longer periods, $\bar{M}_w$ dramatically decreased to no more than several thousand after 24 h.

Changes in molecular weight distribution (MWD) with time are shown in Figure 2. The MWD peak was located at several hundred thousand at 6 h, that is, at the time

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