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Notes

Synthesis of Poly[1-(trimethylsilyl)-1-propyne] with Extremely High Molecular Weight by Using $TaCl_5$–Ph_3Bi (1:1) Catalyst[1]

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Recently, not only the polymerization of acetylene but also that of substituted acetylenes has been intensively studied.[3] We have succeeded in the synthesis of various substituted polyacetylenes.[4] 1-(Trimethylsilyl)-1-propyne [$CH_3C{\equiv}CSi(CH_3)_3$] polymerizes with the pentahalides of tantalum and niobium ($TaCl_5$ and $NbCl_5$) alone [2b,5] to give a new polymer having weight-average molecular weights ($\bar{M}_w$'s) of 1×10^5–1×10^6. Poly[1-(trimethylsilyl)-1-propyne] is white, soluble, air-stable, and electrically insulating, which gives a striking contrast to the properties of polyacetylene. Further, this polymer has proved to exhibit the highest oxygen permeability among all the existing polymers.[5,6]

Organometallics of group 4 and 5 main-group metals (e.g., Ph_4Sn, Et_3SiH, Ph_3Bi) work as weak reducing agents and eventually play important roles as cocatalysts in the polymerization of substituted acetylenes by group 5 and 6 transition-metal catalysts. For instance, the polymerization of disubstituted acetylenes (e.g., 1-phenyl-1-propyne, 2-octyne, 1-chloro-2-phenylacetylene) by WCl_6 or $MoCl_5$ yields polymers only in the presence of these cocatalysts.[4] As another example, polymer degradation occurs in the polymerization of 1-phenyl-1-propyne by $TaCl_5$ and $NbCl_5$, whereas it is restrained in the presence of the cocatalysts, resulting in the formation of high molecular weight poly(1-phenyl-1-propyne).[7]

Here we report the synthesis of high molecular weight poly[1-(trimethylsilyl)-1-propyne] with a catalyst system composed of a equimolar mixture of $TaCl_5$ and Ph_3Bi [1:1 $TaCl_5$–Ph_3Bi]. In the course of our study on the cocatalyst effect, it was found that the $TaCl_5$–Ph_3Bi catalyst achieves extremely high $\bar{M}_w$, up to 4×10^6. This molecular weight is the highest among those of the substituted polyacetylenes ever known.[3,4] The influences of various cocatalysts and polymerization conditions are also discussed.

Results and Discussion

Table I shows the effect of various cocatalysts on the polymerization of 1-(trimethylsilyl)-1-propyne by $TaCl_5$ and $NbCl_5$. Polymerizations were run in toluene at 80 °C for 24 h. $TaCl_5$ alone yielded quantitatively poly[1-(trimethylsilyl)-1-propyne] having a $\bar{M}_w$ somewhat lower than 1×10^6 [$\bar{M}_w$'s and number-average molecular weights ($\bar{M}_n$'s) were determined by gel permeation chromatography (GPC)]. It is of great interest that an equimolar mixture of $TaCl_5$ and Ph_3Bi afforded the polymer with $\bar{M}_w$ as high as 4×10^6 without reducing the polymer yield. Organoantimony, -tin, and -silicon cocatalysts also increased the $\bar{M}_w$ of the polymer to ca. 1.5×10^6–3.5×10^6 but reduced somewhat the polymer yield.

Table I
Polymerization of 1-(Trimethylsilyl)-1-propyne by Various $TaCl_5$- and $NbCl_5$-Based Catalysts[a]

catalyst	polymer[b] yield, %	$\bar{M}_w \times 10^{-4}$ [c]	$\bar{M}_n \times 10^{-4}$ [c]
$TaCl_5$	100	84	19
$TaCl_5$–Ph_3Bi	100	400	180
$TaCl_5$–Ph_3Sb	86	360	150
$TaCl_5$–Ph_4Sn	88	240	100
$TaCl_5$–n-Bu_4Sn	51	280	77
$TaCl_5$–Ph_3SiH	83	170	72
$TaCl_5$–Et_3SiH	65	260	100
$NbCl_5$	100	32	22
$NbCl_5$–Ph_3Bi	84[d]		
$NbCl_5$–Ph_4Sn	22[d]		
$NbCl_5$–Ph_3SiH	35[d]		

[a] Polymerized in toluene at 80 °C for 24 h; $[M]_0$ = 1.0 M, [cat] = [cocat] = 10 mM. [b] Methanol-insoluble products; the polymer yields agreed with the monomer conversions. [c] Determined by GPC. [d] Virtually insoluble in toluene.

The polymer produced with 1:1 $TaCl_5$–Ph_3Bi under the conditions given in Table I completely dissolved in such solvents as toluene and chloroform. The GPC curve of this polymer was unimodal, and its dispersity ratio ($\bar{M}_w/\bar{M}_n$) was ca. 2. These mean that the molecular weight distribution is the most probable distribution and that the polymerization proceeds in a homogeneous system.

In the case of the $NbCl_5$ catalyst by itself, the polymer formed was totally soluble in toluene. In general, however, the polymers obtained in the presence of cocatalysts were virtually insoluble (Table I). This insolubility might be based on a difference in the geometric structure of the main chain.

Use of Ph_3Bi as a cocatalyst appreciably accelerates the polymerization by $TaCl_5$ to achieve 100% yield within 30 min under the conditions shown in Figure 1.[8] Unlike the case of 1-phenyl-1-propyne,[7] polymer degradation is not observed, irrespective of the presence or absence of Ph_3Bi. The addition of the cocatalyst increases the $\bar{M}_w$ of polymer by about 5 times. This result indicates that a more active propagating species forms in a smaller quantity in the polymerization by the $TaCl_5$–Ph_3Bi catalyst than that in the polymerization by $TaCl_5$ alone. Though the active species formed from the $TaCl_5$–Ph_3Bi catalyst has not been identified, probably Ph_3Bi will reduce $TaCl_5$ to form an active species which contains a moiety of Ph_3Bi, propagates quickly, and hardly undergoes the transfer and termination reactions.

Solvent effects on the polymerization were examined by using $TaCl_5$–Ph_3Bi, which had achieved the highest $\bar{M}_w$. Polymer yield reached 100% in the hydrocarbon and halogenated hydrocarbon solvents shown in Table II. The polymers obtained in cyclohexane and 1,2-dichloroethane, however, were partly insoluble, and the $\bar{M}_w$ of the polymer formed in chlorobenzene was lower than that in toluene.

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Table II
Effects of Solvent and Temperature on the Polymerization of 1-(Trimethylsilyl)-1-propyne by 1:1 $TaCl_5$–Ph_3Bi[a]

solvent	temp, °C	polymer[b] yield, %	$\bar{M}_w \times 10^{-4}$[c]	$\bar{M}_n \times 10^{-4}$[c]
toluene	80	100	400	180
cyclohexane	80	100[d]		
PhCl	80	100	210	59
$(CH_2Cl)_2$	80	100[d]		
toluene	0	64[d]		
toluene	30	90[d]		
toluene	60	95	250	130
toluene	100	100	300	140
xylene	130	100	220	95

[a] Polymerized for 24 h; $[M]_0$ = 1.0 M, [cat] = [cocat] = 10 mM. [b] Methanol-insoluble products; the polymer yields agreed with the monomer conversions. [c] Determined by GPC. [d] Partly insoluble in toluene.

Consequently, toluene appears to be the most suitable polymerization solvent.

The polymerization by $TaCl_5$–Ph_3Bi was examined at different temperatures in a range of 0–130 °C. The polymers formed at 30 °C or below were partly insoluble in toluene. At 60 °C or above, totally soluble polymers were obtained in virtually quantitative yields. The $\bar{M}_w$ of the polymer showed a maximum at 80 °C.

Table III shows results for the effect of monomer-to-catalyst ratio ($[M]_0/[TaCl_5]$) in toluene with fixing the cocatalyst-to-catalyst ratio ($[Ph_3Bi]/[TaCl_5]$) at unity. The polymer yield was practically quantitative when the monomer-to-catalyst ratio was in a range of 12.5 to 100, whereas the yield sharply decreased when the ratio was raised to 200 or higher. With increasing monomer-to-catalyst ratio, $\bar{M}_w$ increased monotonously to reach ca. 5 $\times 10^6$ at the ratio of 200.

When the cocatalyst-to-catalyst ratio was changed from 0.25 to 4.0, the polymer yield was always ca. 100%, while the $\bar{M}_w$ showed a maximum of 4 $\times 10^6$ at the ratio of unity (Table III).

Intrinsic viscosities ($[\eta]$'s) of some polymers are shown in Table III. The following $[\eta]$ vs. $\bar{M}_w$ or $\bar{M}_n$ relationships were obtained by the least-squares treatment of the data in Table III:

$$[\eta] = 1.00 \times 10^{-5}\bar{M}_w^{0.931} \quad ([\eta] \text{ in dL·g}^{-1})$$

$$[\eta] = 2.75 \times 10^{-5}\bar{M}_n^{0.913} \quad ([\eta] \text{ in dL·g}^{-1})$$

The exponent values of 0.931 and 0.913 are clearly larger than those (0.5–0.8) for most vinyl polymers. This indicates that this polymer is taking a more expanded conformation in solution than are vinyl polymers. The expanded conformation is thought to originate from the stiff polymer chain due to both the alternating double-bond structure and the presence of bulky substituents.

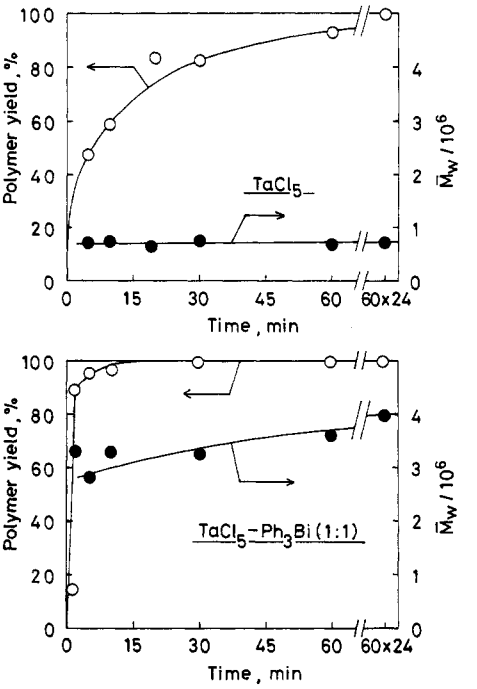

Figure 1. Time dependences of polymer yield and M_w in the polymerization of 1-(trimethylsilyl)-1-propyne by $TaCl_5$-based catalysts in toluene at 80 °C; $[M]_0$ = 1.0 M, [cat] = 20 mM ($TaCl_5$) or 10 mM ($TaCl_5$–Ph_3Bi).

As seen in Table III, the high $\bar{M}_w$'s of 4.0 $\times 10^6$ and 4.9 $\times 10^6$ are endorsed by large $[\eta]$ values of 13.2 and 17.0, respectively. To our knowledge, these $\bar{M}_w$ and $[\eta]$ values are higher than any other values so far reported for substituted polyacetylenes.[3,4]

Experimental Section

A typical polymerization procedure is as follows (cf. Table I, $TaCl_5$–Ph_3Bi system): Under dry nitrogen, $TaCl_5$ (0.10 mmol, 36 mg), Ph_3Bi (0.10 mmol, 44 mg), and toluene (5.0 mL) were mixed and allowed to stand (aged) at 80 °C for 15 min. To this catalyst solution was added a mixture of 1-(trimethylsilyl)-1-propyne (10 mmol, 1.12 g, 1.48 mL) and toluene (3.5 mL) at 80 °C. Polymerization was run at 80 °C for 24 h and then terminated with a mixture (2 mL) of toluene and methanol (volume ratio 4:1). The reaction mixture was diluted with toluene (200 mL) and poured into a large excess (3 L) of methanol under stirring. The polymer formed was filtered and dried. The polymer yield was 100% according to gravimetry (the monomer conversion was determined by gas chromatography when necessary).

The values of $\bar{M}_w$ and $\bar{M}_n$ were determined tentatively by GPC on a Jasco Triroter chromatograph, eluent $CHCl_3$. A series of

Table III
Effects of Monomer, Catalyst, and Cocatalyst Concentrations on the Polymerization of 1-(Trimethylsilyl)-1-propyne by $TaCl_5$–Ph_3Bi[a]

$[M]_0$, M	$[TaCl_5]$, mM	$[Ph_3Bi]$, mM	$[M]_0/[TaCl_5]$	polymer[b] yield, %	$\bar{M}_w \times 10^{-4}$[c]	$\bar{M}_n \times 10^{-4}$[c]	$[\eta]$,[d] dL·g^{-1}
0.25	20	20	12.5	90	160	67	5.9
0.50	20	20	25	100	190	66	5.5
0.50	10	10	50	100	280	130	10.1
1.0	10	10	100	100	400	180	13.2
1.0	5.0	5.0	200	65	490	190	17.0
1.5	5.0	5.0	300	0			
1.0	10	40	100	95	230	120	
1.0	10	20	100	100	190	100	8.7
1.0	10	5.0	100	100	260	140	10.0
1.0	10	2.5	100	100	300	150	

[a] Polymerized in toluene at 80 °C for 24 h. [b] Methanol-insoluble products; the polymer yields agreed with the monomer conversions. [c] Determined by GPC. [d] Measured in toluene at 30 °C.

polystyrene gel columns, Shodex A802, A804, A806, and A807 (Showa Denko, Co., Japan) was used, whose exclusion limit molecular weight had been estimated to be ca. 2×10^8. The calibration curve for $\bar{M}_w$ and $\bar{M}_n$ calculations was obtained with 10 monodispersed polystyrenes whose $\bar{M}_n$'s were in a range 3.7×10^4–6.8×10^6. Intrinsic viscosities were measured in toluene solution at 30 °C.

Registry No. $(CH_3)_3SiC{\equiv}CCH_3$ (homopolymer), 87842-32-8; $TaCl_5$, 7721-01-9; Ph_3Bi, 603-33-8; Ph_3Sb, 603-36-1; Ph_4Sn, 595-90-4; Bu_4Sn, 1461-25-2; Ph_3SiH, 789-25-3; Et_3SiH, 617-86-7; $NbCl_5$, 10026-12-7.

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(8) The time course of intrinsic viscosity in the polymerization by $TaCl_5$ was reported.[2b] Here the time–$\bar{M}_w$ relationship is shown for comparison.

Ferroelectric Properties of a Copolymer of Vinylidene Fluoride and Trifluoroethylene Blended with Poly(methyl methacrylate)

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Random copolymers of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) are known to exhibit many features characteristic of ferroelectrics.[1-6] Although domain structures have not been observed so far, the system shows distinct transitions in its properties near the Curie temperature, T_c. For example, as the temperature approaches T_c from below, both the remanent polarization and the piezo- and pyroelectric activities drop sharply to zero,[1-4] the electric susceptibility exhibits a temperature dependence in accordance with the Curie–Weiss law,[1,6] and the molecular conformation changes from the trans-zigzag form to the gauche form;[7,8] furthermore, there is an increase in the crystal lattice spacing[1] as well as a change in the specific heat.[5] In addition to these transition phenomena, the copolymer system displays a wide variation in the melting point over the entire range of composition.[9] Since the conformational change at T_c primarily arises from intramolecular interactions whereas the melting behavior involves both intra- and intermolecular interactions, it is of interest to examine how the ferroelectric and other properties of the copolymers may be affected by mixing them with a compatible polymer. In this paper, we report the results of a brief study made on the blends of P(VDF/TrFE) and poly(methyl methacrylate) (PMMA),

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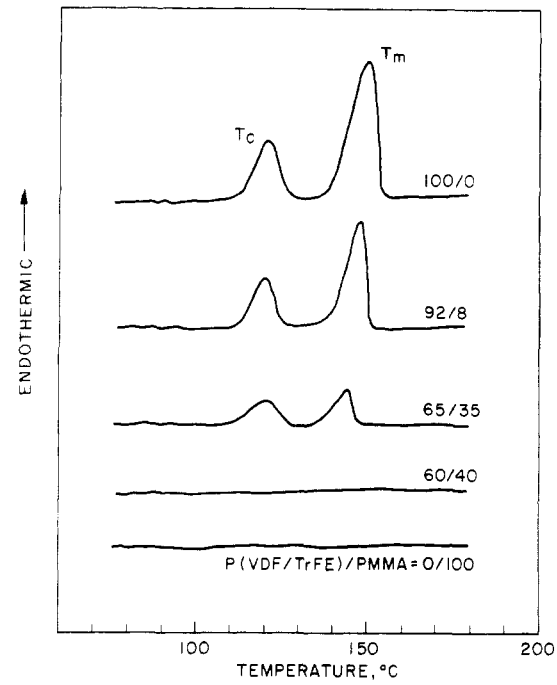

Figure 1. DSC thermograms of P(VDF/TrFE), PMMA, and their mixtures obtained at the scanning rate of 20 °C/min.

which have been found to be mutually compatible in the melt state. While our study was inspired by a previous investigation on blends of poly(vinylidene fluoride) (PVDF) and PMMA,[10] the homopolymer PVDF does not display ferroelectric transitions below its melting point; therefore, it does not allow us to carry out the type of study described in this paper.

Experimental Section

A copolymer of vinylidene fluoride and trifluoroethylene (P(VDF/TrFE)) having a molar compositional ratio of 78.5/21.5 was kindly supplied by Central Glass Co., Japan. It had an $\bar{M}_n$ value of 6.73×10^4 and a polydispersity of 2.18. Atactic PMMA with an $\bar{M}_n$ of 1.27×10^4 and a polydispersity of 2.18 was supplied by Mitsubishi Rayon Co. Ltd., Japan.

Films of P(VDF/TrFE), PMMA and their mixtures were cast from *N,N*-dimethylacetamide solution (3 g/100 mL) onto glass substrates maintained at 60 °C and subsequently allowed to dry slowly at room temperature. The average thickness of the films was about 80 μM. Unless otherwise noted, the compositional ratio of P(VDF/TrFE) to PMMA will be reported on the weight basis.

Calorimetric study was carried out with a Rigaku-Denki Model PTA-10 differential scanning calorimeter. Prior to temperature scanning, each sample (ca. 5 mg) was heated at 200 °C for 30 min to ensure complete melting of crystals and then cooled to room temperature at a rate of 10 °C/min.

Measurements of the piezoelectric constant were made at a frequency of 10 Hz with an apparatus described in ref 11. Films for these measurements were first metalized with aluminium electrodes (ca. 100 nm thick) on opposite faces in the central region covering an area of 5×8 mm^2 and subsequently poled at 100 °C under a dc field of 20 MV/m for 30 min.

Results and Discussion

Thermograms of P(VDF/TrFE), PMMA, and several of their blends obtained at a heating rate of 20 °C/min are shown in Figure 1. As expected,[4,9] the copolymer itself exhibits two prominent endothermic peaks; the one at 150.5 °C corresponds to the melting event while the other at 120 °C corresponds to the Curie transition.[4,9] When PMMA is added to the copolymer, both peaks diminish progressively and disappear completely as the PMMA content, ϕ_w, exceeds 40 wt %; however, while the melting point shifts continually toward lower temperatures, the

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