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Polymerization of Butadiene in Polystyrene with a Homogeneous Ziegler–Natta Catalyst

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ABSTRACT: Polybutadiene–polystyrene blends have been prepared with two Ziegler–Natta catalysts, titanium tetrabutoxide–triethylaluminum and vanadium(III) acetylacetonate–triethylaluminum, by an in situ polymerization technique. The polybutadiene synthesized with the titanium catalyst within the polystyrene matrix had a higher cis-1,4 content than did solution-polymerized polybutadiene. This difference decreases as the temperature of polymerization increases and appears to be related to the stiffness of the matrix. X-ray fluorescence and transmission electron microscopy proved that the polybutadiene was evenly distributed across the thickness of the blends. Phase-separated domains with sizes varying from 500 to 2000 Å existed in these materials. This size is smaller than observed in high-impact polystyrene.

Introduction

During the last decade research on polymer blends has increased significantly as evidenced by several books[1-3] and reviews[4,5] on the subject. Much of this research has focused on the thermodynamic aspects of these materials. Recently research has, however, been done on the preparation of blends by an in situ technique which involves the polymerization of a monomer within a polymeric matrix. This is distinct from interpenetrating networks (IPN) in that the matrix is neither swollen nor cross-linked. In some instances this area offers several advantages over conventional methods of preparing blends.

In the conductive polymer field this technique has been used to prepare new blends. Galvin and Wnek[6] were able to prepare polyacetylene blends in polyethylene and poly(ethylene oxide). These blends were mechanically tough and highly conductive at a few percent polyacetylene when oxidized with iodine. This contrasts with blends prepared by solution casting that were not conductive at 40% polyacetylene. This difference has been attributed to smaller domain sizes that resulted from the in situ technique.

Walsh and co-workers[7-9] used this technique to prepare several blends including poly(vinyl chloride) (PVC) in solution-chlorinated polyethylene (SCPE) and PVC in poly(*n*-butyl acrylate). After synthesis the blends were examined for thermodynamic compatibility. This preparation technique was chosen because it can eliminate questions about solvent influences on compatibility. For example, if a blend of PVC in SCPE is prepared by solution casting from tetrahydrofuran or methyl ethyl ketone, it is a one-phase structure. When cast from dichloromethane the films exhibit two-phase behavior. Studies done on mechanically mixed blends were also conflicting.[9] In situ preparation of the blends allowed Walsh and co-workers to conclude that the polymers were thermodynamically compatible at ambient temperature.

Yau and Stupp[10] have polymerized methyl methacrylate by a free radical process in solid matrices of stereoregular poly(methyl methacrylate) (PMMA). The configurational disorder of the in situ polymerized methyl methacrylate was found to depend on the ratio of methyl methacrylate monomer to PMMA. At low ratios where the swelling of the matrix was limited, two observations were noted. First the number of heterogeneous triads increased independent of the tacticity of the matrix PMMA. The second observation depended on the matrix tacticity. If the matrix was isotactic PMMA, the number of syndiotactic triads increased. If the matrix was highly syndiotactic PMMA, the number of isotactic triads increased slightly. When a less stereoregular PMMA was utilized as the matrix, tacticity did not depend on this ratio. These results are consistent with the occurrence of a replica effect[11-14] in the solid matrices.

In summary, in situ polymerization is a useful synthetic technique. It has been used to prepare novel polymer blends and has potential applications for modifying polymer surfaces. It has also provided insight into the physics of polymer blends and the chemistry of polymerization. A considerable amount of basic research is still, however, needed in this field. We have, therefore, chosen to investigate a model system, i.e., polystyrene–polybutadiene. The aim of our research was to address two questions. First, how does the chemistry of a Ziegler–Natta catalyst change when the solvent for the reaction is a solid? Second, if the two polymers are thermodynamically in-

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compatible can the phase separation be limited by polymerization within a solid matrix below its glass transition temperature?

Experimental Section

Materials. Butadiene (Matheson Research Grade 99.8%) was passed through a column of NaOH pellets followed by a column of 4Å molecular sieves. The monomer was then vacuum distilled from dibutylmagnesium. Before polymerization a 2-L gas bulb was filled with purified butadiene to 1 atm. Purification was completed with three freeze–pump–thaw cycles on the monomer in the gas bulb. The titanium tetrabutoxide [$Ti(OBu)_4$] (Aldrich) was distilled under vacuum while triethylaluminum (Et_3Al) (Alfa) and vanadium(III) acetylacetonate [V^{III}(acac)] (Aldrich) were used as received. Toluene was distilled over calcium hydride under a dry, oxygen-free argon atmosphere. Polystyrene (PS) (Aldrich $\bar{M}_w$ = 209 000) was dissolved in toluene and precipitated in hexane. Following filtration it was dried in a vacuum oven at 70 °C. It was then outgassed on a vacuum line to 1×10^{-4} atm.

Synthesis of Polystyrene–Polybutadiene (PS–PB) Blends. A detailed description of this synthesis has been previously published.[15] For continuity a brief description will be given in this paper. The Ziegler–Natta catalysts were prepared in a Dri-Lab by adding 1.35 mL of $Ti(OBu)_4$ or 1.38 g V^{III}(acac) to 15 mL of toluene. This was followed by a slow addition of 3.26 mL of Et_3Al to the Ti catalyst or 2.2 mL of Et_3Al to the vanadium catalyst. Both catalysts were allowed to age for 30 min before 0.25 mL of catalyst solution was added to a solution of 1.5 g of polystyrene in toluene. A film of polystyrene–catalyst was cast overnight in the Dri-Lab. The next morning the film was outgassed on the vacuum line for at least 2 h. After outgassing the films contain some residual toluene (2 to 5 wt %). To remove all of the toluene would require heating the films under vacuum for several days. These high temperatures might effect the catalyst, therefore, this was not performed. To initiate polymerization the polystyrene–catalyst film was exposed to butadiene gas on a submanifold of the vacuum line. A manometer attached to the submanifold allowed us to monitor the composition of the blend. When the correct composition was achieved the polymerization was terminated by condensing the butadiene into the gas bulb with liquid N_2 and outgassing the film.

Solution polymerizations were run as controls. In these cases 0.5 mL of catalyst solution, 3.0 g of PS, and 20 mL of toluene were placed in a reaction vessel. After a freeze–pump–thaw cycle to remove argon, the solution was exposed to butadiene.

Characterization of the Blends. NMR. NMR spectra were recorded at 45 °C on a Varian XL 200 spectrometer with a ^{13}C frequency of 50.3 MHz. Since some cross-linking occurred in the 1,2-polybutadiene, the blends were sonicated at −78 °C in deuteriated chloroform. Cross checks with IR analysis confirmed that sonication did not influence our results. The NMR spectra were proton decoupled with a 3.5-s delay between pulses to allow for more acquisitions and a better signal-to-noise ratio. Control spectra collected with longer delays (10 s) and no nuclear Overhauser enhancement (NOE) proved that within experimental error quantification of butadiene was not affected. However, the resolved polystyrene resonances were not enhanced as fully as the butadiene resonances. The overall butadiene composition in the blends was, therefore, determined by weight differences not by ^{13}C NMR.

Differential Scanning Calorimetry (DSC). Thermoanalysis was performed on a Perkin-Elmer DSC-4 in sealed volatile pans that prevented loss of residual toluene. The samples were scanned from −100 to 120 °C at a rate of 20 °C/min. At the end of the first scan the samples were held at 120 °C for 15 min. They were then quenched to −100 °C and rescanned.

Transmission Electron Microscopy (TEM). The blends were cryogenically microtomed with a Du Pont Sorvall MT 6000 microtone. To provide contrast the polybutadiene was stained with OsO_4 from the vapor for 24 h. The specimens were examined on a JEOL 100-CX electron microscope at 100 keV.

Results and Discussion

Chemistry of the Catalysts. As noted in our previous paper,[15] the structure of the polybutadiene polymerized in solid polystyrene with the Ti catalyst depended on the temperature of the polymerization reaction. Table I, which contains compositions obtained from ^{13}C NMR experiments, summarizes this data. The values reported are a ratio of the cis-1,4 peak to the total of the cis-1,4 and 1,2 peaks. The areas under defect peaks were not calculated for these tables. The values do not, therefore, represent the absolute percent of 1,2 or cis 1,4 in the polymer. At ambient temperature the percent *cis*-1,4-polybutadiene is much higher in the in situ polymerized butadiene than it is in the solution-polymerized butadiene. As the polymerization temperature increases toward the glass transition temperature of polystyrene, the percent cis 1,4 decreases to 16%. This is close to the value found in the solution polymerization of butadiene. Since the cis-1,4 content in solution polymerization is essentially the same over this temperature range, the differences in the in situ cases cannot be explained by temperature effects on the catalyst.

Table I
Polybutadiene Temperature versus Temperature for in Situ Polymerized and Solution Polymerized Butadiene Using the Ti Catalyst

butadiene polymerized in solid PS		butadiene polymerized in a toluene solution of PS	
temp, °C	% cis 1,4	temp, °C	% cis 1,4
22	28 ± 1	22	13 ± 2
50	18	50	11
70	16	70	11

Table II
Polybutadiene Structure as a Function of Pressure for Solution Polymerizations with Dissolved Polystyrene

pressure	% cis 1,4	pressure	% cis 1,4
0.85 atm	13 ± 2	0.1 atm	15
0.2 atm	14		

One variable that could be different for the in situ polymerizations at lower temperatures is the concentration of monomer around the catalyst site. Hirai et al.[16] have proposed that the active site for 1,2-polymerization with this catalyst has two π-allyl butadiene groups and one alkoxy group coordinated to Ti^{III}. If the monomer concentration dropped low enough this site might not form. At ambient temperature the diffusion of monomer into the matrix should be slower than in either solution polymerizations or in matrices at elevated temperatures. To mimic the condition that occurs during in situ polymerization at low temperatures, we decreased the pressure of butadiene gas used in a solution polymerization. These reactions were run without stirring to keep the concentration of butadiene in solution as low as possible. ^{13}C NMR spectra were recorded for these polymerizations and the percent cis 1,4 was calculated. The results appear in Table II. As the pressure is lowered the percent cis 1,4 shows no significant difference. It is possible that the concentration in the films is lower than in our lowest solution polymerization, but at this time we have not measured that value. We, therefore, cannot eliminate concentration of monomer around the catalyst site as the cause of lower stereoregularity in the films.

Since the lower stereoregularity cannot be conclusively attributed to either temperature effects or concentration of the monomers, it seems that the rigidity of the polystyrene matrix might be the cause. As a control, a film with dead catalyst was exposed to butadiene gas. After 2 days the film had taken up 1 wt % butadiene. The thickness of the film was not changed by the butadiene, indicating that these films are indeed rigid and not swollen by the monomer. At higher temperatures the matrix is

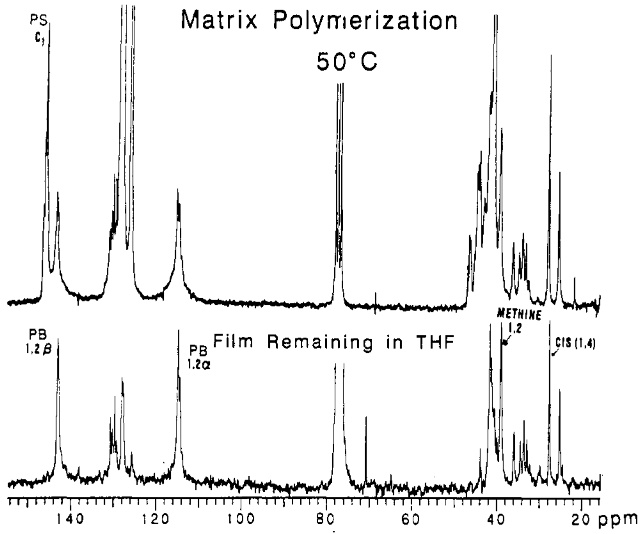

Figure 1. ^{13}C NMR spectra of a 30% PB–70% PS blend before and after extraction with THF.

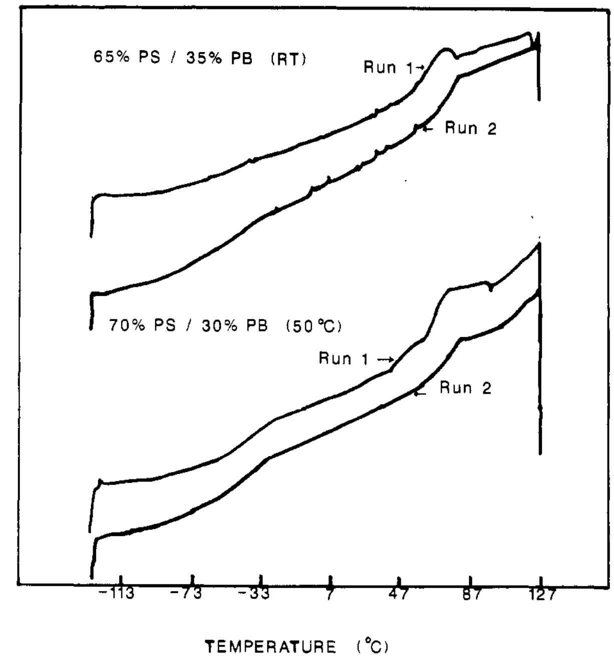

Figure 2. DSC scans of two PS–PB blends prepared by in situ polymerization. The upper set of scans are for a room temperature blend, while the lower set correspond to a 50 °C blend. The first scan in each set is for the blend as prepared. The second run is after annealing at 120 °C for 15 min.

more mobile, accounting for more solution-like behavior. It should also be noted that when the percent polybutadiene in the blend increases from 20 to 35 wt % the cis-1,4 content decreases to 22% at ambient temperature. At this composition the catalyst site is probably surrounded by polybutadiene as opposed to polystyrene. The catalytic process could be behaving more like a solution polymerization due to increased mobility around the site (PB has a T_g well-below room temperature) or to a higher diffusion of butadiene gas through the polybutadiene. The solubility parameter of butadiene ($\delta = 7.1$)[17] is closer to that of polybutadiene ($\delta = 8.1–8.6$)[2] than to that of polystyrene ($\delta = 8.5–9.3$).[2] At higher conversions when the polybutadiene begins to form a continuous phase, the monomer would be more soluble in this phase and might preferentially diffuse through it. We know that when a 30% blend is exhaustively extracted with tetrahydrofuran, a continuous film of polybutadiene is left. Since the T_g of polybutadiene is below room temperature, diffusion through this phase might be faster.

Additional work with the $V^{III}(acac)–Et_3Al$ catalyst reveals that the butadiene stereoregularity is not affected by the use of polystyrene as the solvent. Blends prepared at room temperature have 12% cis-1,4 linkages while butadiene polymerized in a toluene solution of this catalyst has 13% cis 1,4. If we could understand why the Ti catalyst is affected by a solid solvent it would provide significant insight to the polymerization mechanisms of these catalysts.

The blends prepared by this in situ technique are insoluble in toluene and tetrahydrofuran at high percents of polybutadiene, especially when the Ti catalyst is used. This may be attributed to cross-linking within the 1,2-polybutadiene, which occurs with the Ti catalyst even in solution polymerization.[18] An alternate, but unlikely, possibility would be grafting to polystyrene. To check for this, a blend was immersed in tetrahydrofuran overnight 3 consecutive times with fresh solvent. The film that remained after all the soluble polymer had been extracted was sonicated at −78 °C in chloroform and a ^{13}C NMR spectrum was recorded. Figure 1 compares the spectra before and after extraction. Since there are no signals from the C_1 of polystyrene at 145 ppm, a significant amount of grafting to polystyrene did not occur. The aromatic $C_{2,3}$ and C_4 carbons of polystyrene resonate in a region (126 and 128 ppm) where defect structures in polybutadiene (cis-trans or cis-1,2 linkages) also occur and therefore, it is impossible to tell whether they are present in the spectrum of the extracted film. Due to overlap of the remaining styrene resonances with butadiene resonances, we cannot say anything about the region between 40 and 42 ppm. This data indicate that any significant amount of grafting to polystyrene has not occurred.

Morphology of the Blends. When the composition of polybutadiene in the blends exceeds about 10%, the blends develop a hazy appearance indicative of phase separation. This is expected since PB and PS are known to be thermodynamically incompatible.[19] To investigate the morphology of these blends we used TEM and DSC.

Figure 2 contains the DSC results of PS–PB blends prepared by the in situ technique at ambient temperature and at 50 °C. In the first run of the room temperature blend, there are two distinct glass transitions. The first at −45 °C is in the temperature range expected for polybutadiene synthesized with this catalyst.[20] The second T_g at 63 °C can be attributed to polystyrene. DSC runs of polystyrene–catalyst films, sampled prior to exposure to butadiene, have the same depression of the polystyrene T_g. This depression could in part be due to residual toluene (2–5%) in the film. After annealing at 120 °C for 15 min, the two transitions in the blend shift further apart to −51 and 74 °C, respectively. The shift of the polybutadiene transition to lower temperature is not due to loss of toluene. Such a loss would increase the transition temperature from its plasticized value.

DSC scans of blends prepared at 50 °C were distinctly different from scans of room temperature blends. As seen in Figure 2, there is now a shoulder (49 °C) on the PS transition. We have prepared several blends at 50 °C and they all exhibit this phenomenon. The PB transition is at a slightly higher temperature than in the previous case (−41 versus −45 °C). Both polystyrene transitions, at 49 and 57 °C, are at lower temperatures than the polystyrene transition in the room temperature blend. We do not believe this can be explained by residual toluene since NMR spectra indicate that blends prepared at the two temperatures have the same amount. Upon annealing the

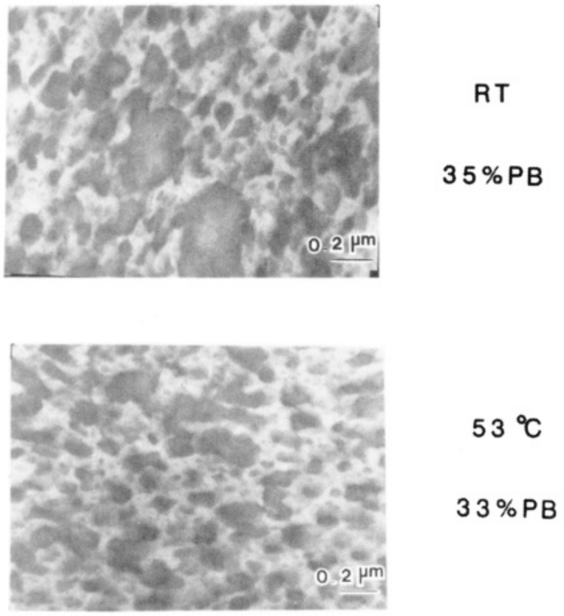

Figure 3. TEM of two PS–PB blends. The upper blend was prepared at room temperature. The lower blend was prepared at 53 °C.

PB transition is lowered to −46 °C while the PS transition is raised to 64 °C. The shoulder totally disappears.

If the systems were homogeneous one glass transition would have been observed. The presence of two transitions that shift apart by a small amount after annealing shows that the blends are phase separated. We are presently conducting studies to determine the significance of the shoulder in the DSC of the 50 °C blend. A question to be addressed is the extent of mixing at the phase boundaries of 50 °C blends as compared to room temperature blends. The data still, however, support the presence of large-scale phase separation in our blends.

TEM and X-ray fluorescence were helpful in elucidating the morphological details of these blends. Linescans were taken for Os, Ti, and Al across the interior of a liquid nitrogen fractured surface. The results from scans across 1 and 41 μm of a 300-μm surface prove that all three elements were present in the interior of these films. In both cases there were no significant fluctuations in the element concentrations across the interior of these films. This suggests that the concentrations of polybutadiene and catalyst are evenly distributed in the center of these films.

Since the in situ technique requires the monomer to diffuse through the film to the catalyst, we expected to see larger concentrations of polybutadiene at the surface of the films. When electron microscopy was performed we found that this was not the case. In almost all blends the polybutadiene appeared to be evenly distributed throughout the polystyrene. In a few blends there was no polybutadiene at the surface. This may be explained by a small leak of oxygen into the film, destroying the surface catalyst.

Micrographs of blends prepared at ambient temperature and 53 °C appear in Figure 3. The domains of polybutadiene in the ambient blend are irregular in shape and vary from 300 to 4500 Å. These sizes are composition dependent, the largest domains varying from 2800 Å at 27 wt % to 4500 Å at 35 wt %. Catalyst sites that remain active for a long time or domains that have coalesced would account for this increase. At the elevated temperature the domain sizes are slightly less heterogeneous, ranging from 300 to 2800 Å for blends of 33 wt %. It is important to remember that while 50 °C is below the starting T_g of these films, it is close to the final polystyrene T_g of the blends (49–57 °C). At this time we cannot say whether the narrower size distribution in the 50 °C blends can be solely attributed to the mobility differences created by the proximity of the polymerization temperature to the final polystyrene T_g. There are alternate explanations. One is a change in the surface tensions of the two polymers as a function of temperature.

After annealing a microtomed section for 15 h under N_2 at 120 °C, the polybutadiene domains increased dramatically (Figure 4). A few domains are now 20 000 Å. This size is closer to what is seen in most PS–PB blends used for impact resistance[21] and is not surprising considering the thermodynamic incompatibility of these polymers. The domain sizes of PB in PS–PB IPNs where both polymers are cross-linked range from 15 to 1200 Å.[22] The fact that our domains are closer in size to those observed in IPNs than in mechanically mixed blends supports the idea that polymerizing in a polymer below its T_g may limit the extent of phase separation. A significant amount of future research is, however, still needed before this will be proven.

In summary we have shown that butadiene can be polymerized in a glassy matrix below the T_g of the matrix. The work also proves that the chemistry of the catalyst can be influenced by the solid solvent. The titanium catalyst was less stereoregular in solid polystyrene, while the vanadium catalyst was unaffected. As such this technique may be a valuable way to study catalyst reactions and mechanisms. It also has applications in preparing new blends and in modifying polymer surfaces. By studying the morphology we determined that smaller domains can be realized without using a cross-linked matrix.. From the data we can also conclude that the second polymer is evenly distributed across the thickness of the film and not confined to the surface. With more time it may be possible to limit or control domain sizes in these

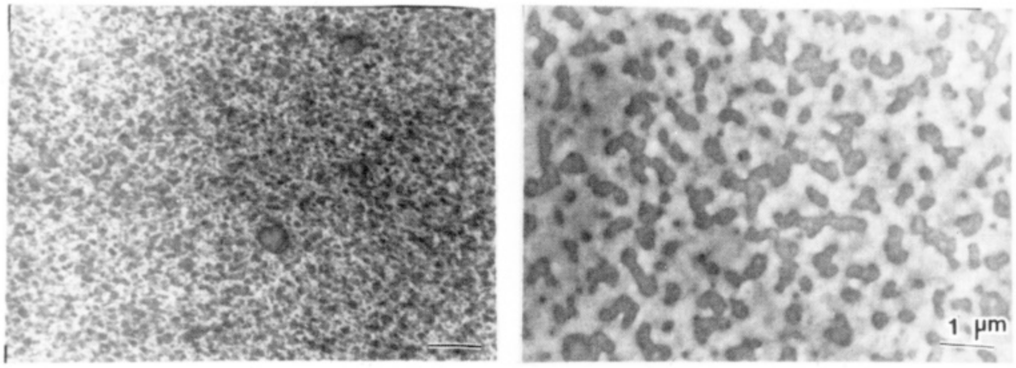

Figure 4. Micrograph on the left is typical of a room temperature PS–PB blend. The micrograph to the right is of the same blend after annealing in N_2 at 120 °C for 15 h. Both micrographs are at the same magnification.

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blends by adjusting parameters such as the difference between the temperature of polymerization and the T_g of the matrix. At present we have demonstrated that this technique can be used to produce blends of immiscible polymers, in which the domain sizes are limited by the slow kinetics of aggregation within a solid.

Registry No. PS, 9003-53-6; PB, 9003-17-2; V^{III}(acac), 13476-99-8; Ti(OBu)$_4$, 5593-70-4; Et$_3$Al, 97-93-8.

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Living Polymerization of 1-Chloro-1-alkynes Catalyzed by MoCl$_5$–*n*-Bu$_4$Sn–EtOH

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ABSTRACT: Polymerization of 1-chloro-1-octyne (ClC≡C-*n*-C$_6$H$_{13}$) catalyzed by a mixture of MoCl$_5$, *n*-Bu$_4$Sn, and EtOH (molar ratio 1:1:0.5) produced a polymer with a narrow molecular weight distribution (MWD; $\bar{M}_w/\bar{M}_n$ = 1.1–1.3). The number-average molecular weight ($\bar{M}_n$) of the polymer increased in direct proportion to conversion and further increased on addition of a new monomer feed to the polymerization system. The ratio of the propagating species to the Mo catalyst was rather small (0.017). Other 1-chloro-1-alkynes (ClC≡CR; R = *n*-C$_4$H$_9$, *n*-C$_8$H$_{17}$, and *n*-C$_{14}$H$_{29}$) formed polymers with similarly narrow MWDs. Thus, the present polymerization indicates the presence of a long-lived propagating species and, though yet imperfect, is the first clear example of living polymerization of acetylenic monomers.

Introduction

Living polymerization is the polymerization in which termination and chain transfer are absent and is a useful technique for the synthesis of tailor-made polymers such as monodisperse polymers and block copolymers. Whereas the living anionic polymerization has been extensively investigated by Szwarc and other researchers,[1] only a few studies have so far appeared on the living polymerization initiated by transition-metal catalysts, i.e., polymerization of norbornene by Ti, Ta, and W catalysts,[2] polymerization of propene by V catalysts,[3] and polymerization of 1,3-butadiene by Ni catalysts.[4] Though the ring-opening polymerization of cyclooctyne was suggested to be a living system, the polymer did not show a narrow molecular weight distribution.[5] Thus there has been no evident report on the living polymerization of acetylenic monomers to date.

Groups 5 and 6 transition-metal (Nb, Ta, Mo, and W) chlorides work as effective catalysts in the polymerization of various substituted acetylenes.[6] Recently, we reported that 1-chloro-1-alkynes (ClC≡CR; R = *n*-C$_4$H$_9$, *n*-C$_6$H$_{13}$, *n*-C$_8$H$_{17}$, and *n*-C$_{14}$H$_{29}$), a series of chlorine-containing aliphatic acetylenes, polymerize with Mo catalysts (e.g., MoCl$_5$–n-Bu$_4$Sn) to give new high-molecular-weight polymers (weight-average molecular weight, $\bar{M}_w$, ca. 2×10^5–2×10^6) in high yields.[7] The molecular weight distributions (MWDs) of the product polymers are, however, rather broad [polydispersity ratio ($\bar{M}_w/\bar{M}_n$) 1.7–2.5].

Mo- and W-catalyzed polymerization of substituted acetylenes and olefin metathesis have many common features (e.g., identical catalysts and cocatalysts effect both reactions). Thus far, a wide variety of catalysts based on W and Mo have been exploited for olefin metathesis.[8–10] Among them, effective catalysts are often composed of three components, that is, WCl$_6$, an organometallic cocatalyst, and a modifier. A number of oxygen-containing compounds can be the modifier. For instance, Calderon et al. have found that a mixture of WCl$_6$, EtAlCl$_2$, and ethanol (EtOH) shows high activity for olefin metathesis, whereas this catalyst is less active if it lacks EtOH.[11]

While we were studying how oxygen-containing compounds would affect the polymerization of 1-chloro-1-octyne by the MoCl$_5$-organometallic cocatalyst system, we found that a three-component catalyst composed of MoCl$_5$, *n*-Bu$_4$Sn, and EtOH produces a long-lived propagating species.[12] The present paper describes a detailed study on the polymerization of 1-chloro-1-octyne and its homologues by MoCl$_5$–*n*-Bu$_4$Sn–EtOH.

Experimental Section

Materials. 1-Chloro-1-alkynes were prepared by lithiation of 1-alkynes, followed by chlorination with tosyl chloride, as described

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