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Synthesis of a *cis*-rich, living poly[(*o*-methylphenyl)acetylene] by use of the $MoOCl_4$–*n*-Bu_4Sn–EtOH catalyst

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Summary

Polymerization of (*o*-methylphenyl)acetylene (*o*-MePA) by $MoOCl_4$-*n*-Bu_4Sn–EtOH catalyst in toluene at 0°C provided a cis-rich living polymer; cis 77%, M_w/M_n = 1.21. The polymerization at -30°C gave results similar to those for 0°C, whereas the polymer obtained at 30°C exhibited a broader molecular weight distribution (MWD) and a lower cis content. Among several organotin compounds, only *n*-Bu_4Sn was effective for the living polymerization of *o*-MePA. The bulkier the alkyl group of alcohols as the third catalyst component, the broader the MWD of the polymer, while the geometrical structure was not affected by the alcohols.

Introduction

In recent years, precise syntheses of polymers are under intensive research.[1] Although stereospecific living polymerization provides the polymers that possess controlled steric structures and narrow molecular weight distributions (MWD), only a few examples of them have been known.[2-6]

Earlier we found that 1-chloro-1-octyne[7] and some ortho-substituted phenylacetylenes[8] polymerize in a living manner in the presence of the $MoOCl_4$–*n*-Bu_4Sn–EtOH (mole ratio 1:1:1) catalyst. Further, we have recently revealed that the polymerization of *tert*-butylacetylene (*t*BA) by the $MoOCl_4$-based ternary catalyst yields a living polymer having a very high stereoregularity (M_w/M_n 1.12, cis ~97%).[6]

The steric structure of the polymer from (*o*-methylphenyl)acetylene (*o*-MePA) can be evaluated by ^{13}C NMR, and it has been found that the polymer obtained with WCl_6 possesses a structure of 41% cis, while the one formed with $MoCl_5$ has 52% cis.[9] In addition, this monomer polymerizes in a living fashion, although the MWD of the polymer is not very narrow (M_w/M_n ~1.25).[10]

In the present study, *o*-MePA was polymerized by Mo-based catalysts, and the steric structure and MWD of the polymers were examined in detail in order to clarify the possibility of synthesizing a stereoregular living polymer.

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Experimental Section

The monomer (*o*-MePA) was prepared according to the literature methods[9,11] [purity >99% by gas chromatography (GC)] . $MoOCl_4$ (Strem Chemicals; purity >99%) was commercially obtained and used without further purification. Toluene as polymerization solvent was washed by the standard method and distilled twice from calcium hydride.

The catalyst solution was prepared as follows: $MoOCl_4$ and an organotin compound were mixed in toluene at a 1:1 mole ratio, and the mixture was aged at 30°C for 15 min. Then an equimolar amount of an alcohol in toluene solution was added, and the mixture was aged at 30°C for an additional 15 min. Polymerizations were initiated by adding a monomer solution to the catalyst solution after keeping them at a given polymerization temperature for 5 min. Polymerizations were quenched with a methanol–pyridine mixture (volume ratio 1:1), and the monomer conversions were determined by GC. The MWDs of the polymers were measured by gel permeation chromatography (GPC; eluent $CHCl_3$; polystyrene calibration). The geometric structure of the main chain of the polymers was determined by ^{13}C NMR (JEOL GSX-270 spectrometer; $CDCl_3$ solution).[9]

Results and Discussion

Effects of the number of catalyst components

Figure 1 shows the conversion and cis contents as a function of time in the polymerization of *o*-MePA. The catalysts used are $MoOCl_4$, $MoOCl_4$–*n*-Bu_4Sn, and $MoOCl_4$–*n*-Bu_4Sn–EtOH. The polydispersity ratios (M_w/M_n) of the polymers obtained with these catalysts after 24 h were 2.85, 1.47, and 1.21 (living polymer), respectively. When $MoOCl_4$ alone was used as catalyst, the monomer was not completely consumed even after 24 h, and the cis content of the polymer was as low as 60% independent of

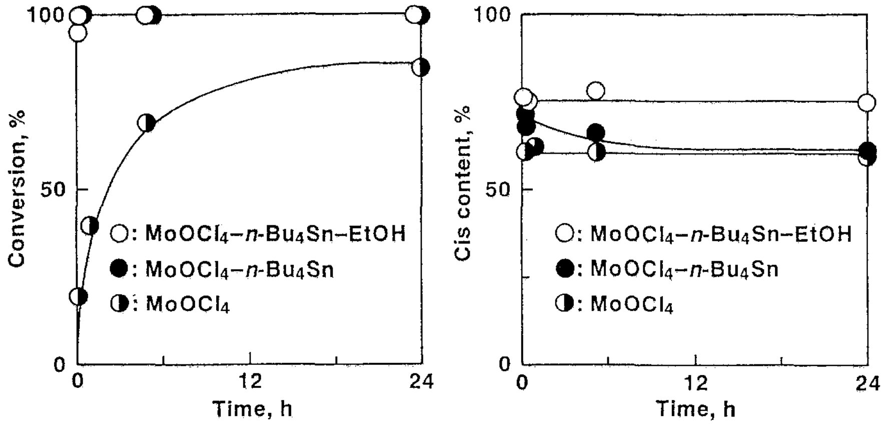

Figure 1. Effects of catalyst components on the polymerization of *o*-MePA by $MoOCl_4$-based catalysts (polymerized in toluene at 0°C; $[M]_0$ = 0.20 M, [Cat] = 10 mM).

polymerization time. On the other hand, the polymerization by the $MoOCl_4$–*n*-Bu_4Sn catalyst was immediately completed; the cis content was 75% at first but gradually decreased to ca. 60%. When the $MoOCl_4$–*n*-Bu_4Sn–EtOH catalyst was employed, the cis content of the polymer was as high as 77%, and virtually constant. As stated below, Lewis acids cause the geometrical isomerization of the main chain. Hence the results regarding the $MoOCl_4$–*n*-Bu_4Sn – EtOH catalyst is attributable to the inhibition of geometrical isomerization by the addition of *n*-Bu_4Sn and EtOH due to reduced Lewis acidity of the polymerizatin system.

Effects of polymerization temperature

Temperature dependence of the methyl signal of ^{13}C NMR spectrum of poly(*o*-MePA) is given in Figure 2. When polymerizations were carried out at 30, 0, and -30°C, the polydispersity ratios of the polymers were 1.35, 1.21, and 1.17, and the cis contents were 66, 77, and 76%, respectively. Thus 0 and -30°C are suitable as polymerization temperature to achieve both narrow MWDs and high cis contents.

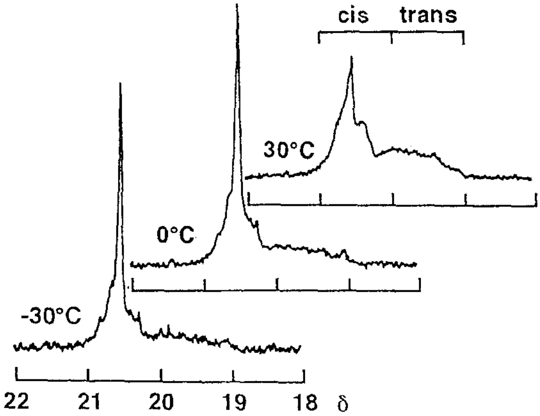

Figure 2. Effect of polymerization temperature on the cis content of poly(*o*-MePA) obtained with $MoOCl_4$–*n*-Bu_4Sn – EtOH (1:1:1) (polymerized in toluene for 1 h; $[M]_0$ = 0.20 M, [$MoOCl_4$] = 10 mM; all the conversions 100%).

In the polymerization of substituted acetylenes by group 5 and 6 transition metal catalysts, the geometric structure of polymers is determined on ring scission of metalacyclobutenes.12) The geometric structure of the polymer formed at 30°C did not depend on the polymerization time. Consequently, the dependence of cis content upon the polymerization temperature might be due to preferential cis formation on the cleavage of the metalacyclobutene at lower temperatures. The reason why cis structure was not exclusively formed is probably that the *o*-methylphenyl group is not so bulky as *tert*-butyl.

Effects of various cocatalysts and alcohols

Table I compiles the results of the polymerization of *o*-MePA using various tetraalkyltins as cocatalysts and alcohols as third components. In the polymerization using Me_4Sn as cocatalyst, the cis content was 75% and as high as the one with *n*-Bu_4Sn, but the polydispersity ratio was 1.72 and larger. The polymerization rate decreased when organotin compounds with bulkier alkyl groups such as isobutyl and isopropyl groups were used. Probably these organotin compounds are not reactive enough, which results in

Table I. Effects of cocatalysts and alcohols on the polymerization of *o*-MePA by $MoOCl_4$–cocatalyst–alcohol (1:1:1) [a]

Cocatalyst	Alcohol	Time, min.	Convn., %	$M_n/10^4$	M_w/M_n	Cis, %
n-Bu_4Sn	EtOH	1	95	3.11	1.21	78
Me_4Sn	EtOH	1	55	4.70	1.72	75
i-Bu_4Sn	EtOH	15	39	—	—	—
i-Pr_4Sn	EtOH	24×60	32	—[b]	—	—
n-Bu_3SnCH_2Ph	EtOH	3×60	77	—[b]	—	—
Ph_4Sn	EtOH	24×60	0	—	—	—
n-Bu_4Sn	MeOH	1	93	4.66	1.16	79
n-Bu_4Sn	EtOH	1	95	3.11	1.21	77
n-Bu_4Sn	*i*-PrOH	1	100	1.83	1.84	77
n-Bu_4Sn	*t*-BuOH	1	12	—[c]	—	—

a) Polymerized in toluene at 0°C; $[M]_0 = 0.20$ M, [Cat] = 10 mM.
b) Partly insoluble in $CHCl_3$. c) Bimodal MWD.

a decrease in the concentration of propagating species. When Ph_4Sn, which has no α hydrogen, was used, *o*-MePA did not polymerize at all.

As the alkyl group of alcohols was made bulkier from methyl to ethyl and isopropyl, the rate of polymerization somewhat increased and the MWDs tended to increase, while the stereoregularity of the polymers hardly changed. On the other hand, *t*-BuOH considerably reduced catalyst activity and brought about a bimodal MWD. The reason is not clear at the moment.

Effects of n-Bu4Sn and EtOH concentrations

In Table II are shown the effects of *n*-Bu_4Sn and EtOH concentrations on the polymerization by $MoOCl_4$–*n*-Bu_4Sn–EtOH, which achieves a narrow MWD and a high cis content. Taking a mole ratio 1:1:1 of catalyst components as a standard, the monomer conversion did not appreciably change with the concentration of *n*-Bu_4Sn, whereas the polymerization rate considerably decreased when the EtOH concentration was increased up to a four-fold excess over $MoOCl_4$. The MWD of polymer was the narrowest (M_w/M_n = 1.21) at a $MoOCl_4$: *n*-Bu_4Sn : EtOH ratio of 1:1:1 and became slightly broader when the concentration of either *n*-Bu_4Sn or EtOH was increased. The cis content of polymer was 77% at $MoOCl_4$: *n*-Bu_4Sn : EtOH = 1:1:1, and was virtually constant or slightly increased when the concentrations of *n*-Bu_4Sn or EtOH were increased.

Table II. Effects of *n*-Bu_4Sn and EtOH concentrations on the polymerization of *o*-MePA by $MoOCl_4$–*n*-Bu_4Sn–EtOH [a)]

Mole ratio [b)]	Time, min	Convn., %	$M_n/10^4$	M_w/M_n	Cis, %
1:1:1	1	95	3.11	1.21	77
1:2:1	1	100	2.22	1.29	77
1:3:1	1	95	2.52	1.29	79
1:4:1	1	87	2.63	1.26	79
1:1:2	1	62	1.73	1.28	78
1:1:3	10	92	2.26	1.29	80
1:1:4	10	61	1.68	1.24	81

a) Polymerized in toluene at 0°C; $[M]_0$ = 0.20 M, $[MoOCl_4]$ = 10 mM.
b) $[MoOCl_4]$: [*n*-Bu_4Sn] : [EtOH].

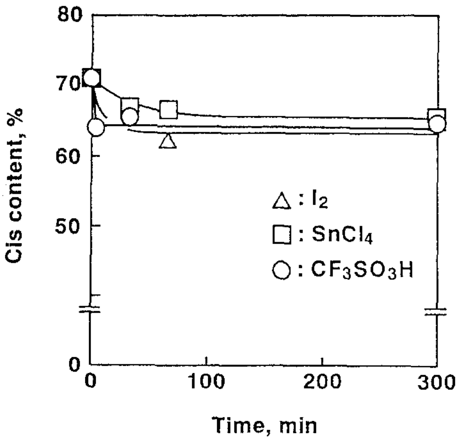

Figure 3. Isomerization of poly(*o*-MePA) by various acids (reacted in toluene at 0°C; [C=C] = 0.20 M, [acid] = 10 mM).

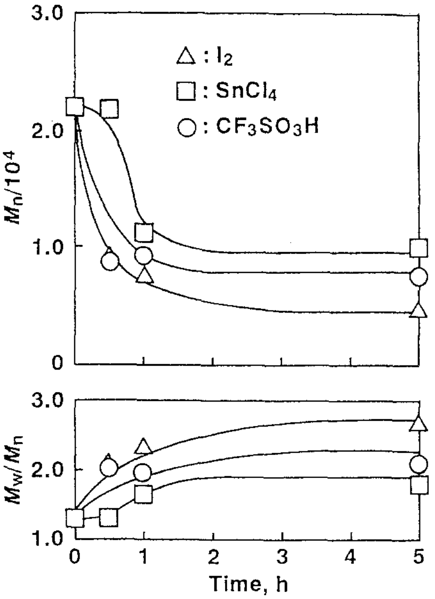

Figure 4. Degradation of poly(*o*-MePA) by various acids (reacted in toluene at 0°C; [C=C] = 0.20 M, [acid] = 10 mM).

Geometrical isomerization and degradation of the polymer

As described above, geometrical isomerization occurred in the polymerization of *o*-MePA by the $MoOCl_4$–*n*-Bu_4Sn catalyst, and eventually the cis content became the same as that with the $MoOCl_4$ catalyst (see Figure 1). In order to clarify whether or not this was due to the Lewis acidity of the polymerization system, the poly(*o*-MePA) obtained with the $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:1) catalyst was treated with Lewis acids (I_2 and $SnCl_4$) and a proton acid (CF_3SO_3H). All these acids caused isomerization, which reached an equilibrium after 1 h (Figure 3). The geometric isomerization was accompanied by a decrease in molecular

weight and broadening of MWD (Figure 4). All of these changes seem to be caused by acids.

Conclusions

The results of the present study are summerized as follows:

i) A living polymer with a fairly high cis content (M_w/M_n = 1.21, cis 77%) was formed with the $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:1) catalyst.

ii) The appreciably high cis content is attributable to the low acidity of the catalyst system.

iii) The reason why poly(*o*-MePA) is less stereoregular than poly(*t*BA) seems the less steric effect of the substituent.

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