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Reactivity of macromonomer in copolymerization of styrene with styrene-terminated macromonomer by $CpTiCl_3$-MAO catalyst

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Summary

The copolymerization of styrene (St) and styrene-terminated macromonomers with $CpTiCl_3$-MAO catalyst was investigated. The contents of the macromonomer in the graft copolymer was found to depend on the miscibility of the macromonomer with the main chain polystyrene formed by copolymerization. miscible system of the syndiotactic polystyrene in the main chain and atactic polystyrene in the side chain was favorable for the incorporation of the macromonomer into the graft copolymer as compared with immiscible system of syndiotactic polystyrene in the main chain and atactic polyisoprene in the side chain. The contents of the SSTM in the graft copolymer was influenced by the MAO/Ti mole ratio and content of the SSTM in the comonomer feed.

Introduction

There are many reports on metallocene polymerizations of various monomers, and novel polymers were synthesized with the metallocene catalysts(1-9). One of the features of metallocene catalysts is capable of incorporating long chain molecules formed during the polymerization. Such examples were found in polymerizations of ethylene(10, 11) and propylene(12-14) with Ti and Zr based metallocene catalyst. This indicates that macromonomers obtained from living anionic polymerizations with a well-defined structure and a narrow molecular weight distribution are able to be utilized as a comonomer in the copolymerization with olefins by metallocene catalysts such as $iPr(Cp)(Flu)ZrMe_2$, $[C_5Me_4\text{-}SiMe_2\text{-}N(t\text{-}Bu)]TiCl_2$ and $CpTiCl_3$. Such copolymerization of propylene with vinyl-terminated styrene macromonomer with constrained geometry catalyst was reported (15). The copolymerization, however, did not give highly stereoregularity on the main chain. On the other hand, in the copolymerization of styrene (St) and styrene terminated macromonomers by syndiospecific polymerization catalysts such as $CpTiCl_3$-MAO catalyst, graft copolymers of highly syndiotactic polystyrene (SPS) on the main chain were synthesized(16).

In the copolymerization of St and styrene terminated polyisoprene macromonomer (SIPM) with $CpTiCl_3$-MAO catalyst, the number of graft chains of the resulting graft copolymer did not exceed over 3 even when a large amount of the SIPM against St was charged in the comonomer feed(17).

On the other hand, the number of the graft chains of the graft copolymer was 12.9 in our briefly reported results for the copolymerization of St and styrene terminated polystyrene macromonomer (SSTM) with the $CpTiCl_3$-MAO(18). Namely, the incorporation of the macromonomer into the graft copolymer was quite different between two copolymerization system, although both macromonomers have the same terminal styrene unit. To clarify the difference in copolymerization behavior, we investigated the copolymerization of St and the STTM with $CpTiCl_3$-MAO catalyst, and the results obtained in this study was compared

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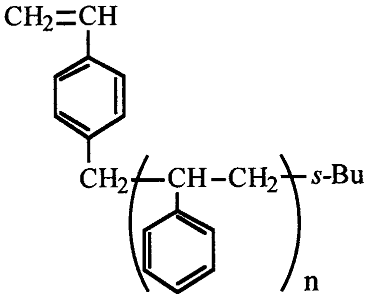
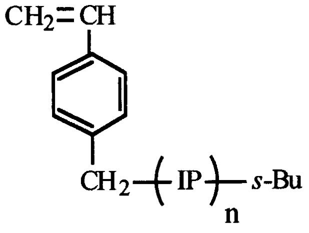
with the reported results for the copolymerization of St and the SIPM(17).



STTM



SIPM

Microstructure of IP units
cis-1,4 : 69.9%
trans1,4 : 23.1%
3,4 : 7.0%
1,2 : 0%

Experimental

Materials

Commercial grade monomers and solvents were purified by conventional methods. sec-Butyllithium purchased from Kanto Chem. Co. as cyclohexane solution, and $CpTiCl_3$ purchased from Aldrich Chem. were used as received. MAO diluted with toluene kindly supplied by the Tosoh-Akzo Chem. Co. was used as received. SSTM was prepared via a living anionic polymerization as previously reported(18). The macromonomer was isolated by a precipitation method using a large amount of methanol from toluene solution, and dried in a vacuum to use the copolymerization.

Copolymerization with St

The copolymerization of St and the SSTM was carried out in a glass tube. After charging the required amount of reagents into the tube by syringe, the tube was sealed under high vacuum at -78°C. After copolymerization, the contents of the tube were poured into a large amount of methanol containing a few percent of hydrochloric acid to precipitate the copolymer formed. The resulting copolymer was extracted by methyl ethyl ketone (MEK) for 12h at 80°C. The polymer yield was determined by gravimetry.

Characterization of the polymers

The structure of the polymers was determined by ^{1}H and ^{13}C NMR spectra of the polymer using a JEOL A-400 spectrometer. The spectra of the polymers were measured in $CDCl_3$ at 30°C, and the MEK-insoluble fraction was taken in o-dichlorobenzene/C_6D_6 at 120°C. The number average molecular weights (M_n) of the STTM were determined by vapor pressure osmometry (VPO) using a Knauer Vapor Pressure Osmometer at 40°C. The M_n of the copolymers and the molecular weight distribution (M_w/M_n) was estimated by GPC using a Tosoh series GPC-8000 at 38°C in THF as calibrated with polystyrene standards. GPC data for the MEK-insoluble fraction was obtained from a Waters GPC 150CV at 120°C in *o*-dichlorobenzene.

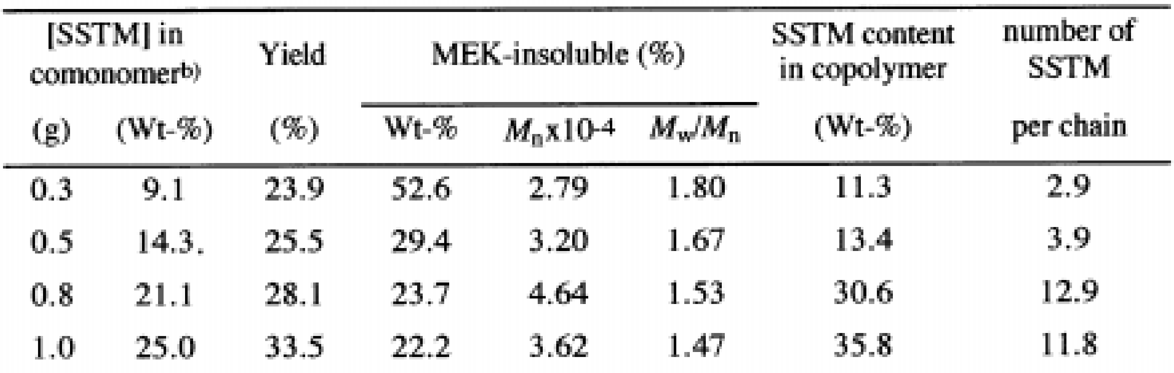
Results and discussion

The contents of SSTM in the syndiotactic graft copolymer

The effects of the SSTM/St ratio in the comonomer feed on the copolymerization of St and SSTM using the $CpTiCl_3$-MAO catalyst were investigated. The results are listed in Table 1.

The resulting copolymers were extracted by MEK, and the MEK-insoluble fraction was confirmed to be syndiotactic graft copolymer by an analysis of the ^{13}C NMR spectroscopy of the graft copolymers(18). The number of grafts per molecule of the graft copolymer was calculated from the peak intensity of the methylene proton of the SPS and of the atactic polystyrene (APS) by the ^{1}H-NMR spectra. Then, the peak intensity ratio of the methylene proton of the APS and the methyl proton of the *s*-Bu group in the SSTM was consistent with the number of the styrene units in the SSTM. Namely, the fraction of the APS in the graft copolymer was corresponded with the grafted SSTM. The SSTM contents in the graft copolymer increased with an increase of the content of the SSTM in the comonomer feed.

Table 1. Graft copolymerization of St and SSTM with $CpTiCl_3$-MAO catalysts in toluene at 50°C for 3h[a)]



[SSTM] in comonomer[b)]		Yield	MEK-insoluble (%)			SSTM content in copolymer	number of SSTM
(g)	(Wt-%)	(%)	Wt-%	M_nx10^{-4}	M_w/M_n	(Wt-%)	per chain
0.3	9.1	23.9	52.6	2.79	1.80	11.3	2.9
0.5	14.3.	25.5	29.4	3.20	1.67	13.4	3.9
0.8	21.1	28.1	23.7	4.64	1.53	30.6	12.9
1.0	25.0	33.5	22.2	3.62	1.47	35.8	11.8

a) [St] = 2.9 mol/L, [Ti] = 4.7 x 10^{-4} mol/L, MAO/Ti = 500 (mole ratio).

b) [SSTM]; M_n = 1100, M_w/M_n = 1.13, f = 0.98.

On the other hand, the molecular weights of the graft copolymer gave a maximum and its molecular weight was 4.64 x 10^{4}. Under this conditions, an maximum number of graft chains per molecule of the graft copolymers was also obtained, and the number of the chains was 12.9. In the copolymerization of St and the SIPM, the number of graft chains was about 3 even when the copolymerization was carried out at high the SIPM content in the comonomer feed(17), i.e., the content of the SSTM in the syndiotactic graft copolymer was higher than that of the SIPM in the syndiotactic copolymerization of St with the STTM and the SIPM.

To clarify this point, we estimated the monomer reactivity ratio of St (M_1) and SSTM (M_2) using the copolymerization equation (1) with the data obtained at low conversion. The conventional Mayo-Lewis equations are reduced to eq. (1) when the mole ratio in the feed is very large, i.e., $[M_1]>>[M_2]$ (19).

$$-d[M_1] / -d[M_2] = (1+r_1[M_1] / [M_2]) / (1+r_2[M_2] / [M_1]) = r_1[M_1] / [M_2]) \qquad (1)$$

The monomer reactivity ratio of St (r_1) was calculated using the observed mole ratio of styrene to SSTM both in the graft copolymer and in the feed monomer by considering the molecular weight of the macromonomer. The r_1 of St thus obtained was estimated to be 0.89, but the mole concentration of the SSTM is much smaller than that of St; the exact r_2 value is difficult to determine. The $1/r_1$ was used to study the copolymerization reactivity of the SSTM(20). The $1/r_1$ was 1.13, which is larger than that of the SIPM ($1/r_1$ = 0.41) in the syndiospecific copolymerization of St (M_1) with the SIPM (M_2) (17). Since the results seems to be difficult to explain with a steric hindrance of the macromonomer. Because we used the macromonomers with same styrene-terminated unit and similar molecular weights. Then, we considered that the crystallization behavior of the graft copolymers originated from the miscibility between the main chain and the side chain. Because, polystyrene (PSt) and polyisoprene (PIP) was immiscible system and SPS and APS is miscible system(21-24). Since the crystallization of SPS is known to be very fast and PSt and PIP are immiscible system, the crystallization of the forming graft copolymer may occurred during the copolymerization. While, SPS and APS are miscible system. Thus, the amount of the STTM in the graft copolymer was higher as compared with that of the SIPM in the copolymer.

To check this point, the DSC measurement was performed, and the charts are shown in Figure 1.

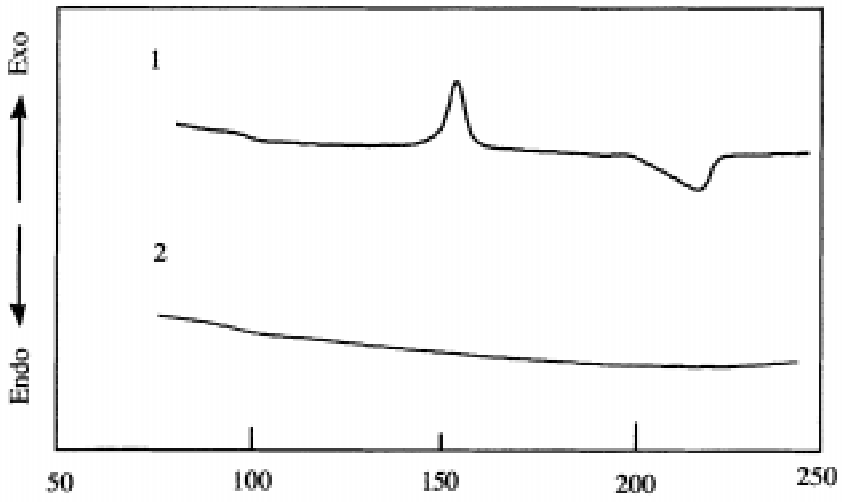


Figure 1. DSC charts for the graft copolymer of (1) poly(st-g-SIPM) SIPM= 25.8 Wt-% and (2) poly(St-g-STTM) STTM=30.6 Wt-%

The graft copolymer of St and the SIPM revealed clear melting point, but the graft copolymer of St and the STTM do not have a clear melting point. This result suggests that the miscibility during the polymerization is correlated with the crystallization of the resulting polymer. Moreover, we observed that the copolymer including of the SIPM was precipitated in the medium due to their crystallization, while the copolymer including the SSTM was swelled in the medium.

In the copolymerizations of propylene with 1-hexene(12, 13), propylene with 1-octene(14) and ethylene with higher olefins(10, 11) by metallocene catalysts, the low crystallinities and the high solubilities of the copolymers in the polymerization medium was reported to be enhanced the copolymerization rate by high rates of diffusion of the monomers to the catalyst center.

It is noted that the reactivity of the SSTM in the syndiotactic copolymerization was lower than that of the small monomer during the radical copolymerization of St ($r_1 = 0.83$) and *p*-methylstyrene, suggesting that the chain stiffness in the main chain and to the steric hindrance of the macromonomer as compared with small molecules decrease the reactivity (25, 26).

Effect of MAO/Ti mole ratio on copolymerization

Figure 2 shows the effects of the MAO/Ti mole ratio on the copolymerization of St and

SSTM using the $CpTiCl_3$-MAO catalyst. The polymer yields and the *M*n of the syndiotactic graft copolymer increased with an increase of the MAO/Ti mole ratio up to 2000. While, in the copolymerization of St and the SIPM, the molecular weight of the resulting syndiotactic graft copolymer decreased with an increase in the MAO/Ti mole ratio(17). This suggests that the difference in the *M*n of the copolymers obtained from both copolymerizations may originate from the difference in the degree of their crystallinities of the polymers.

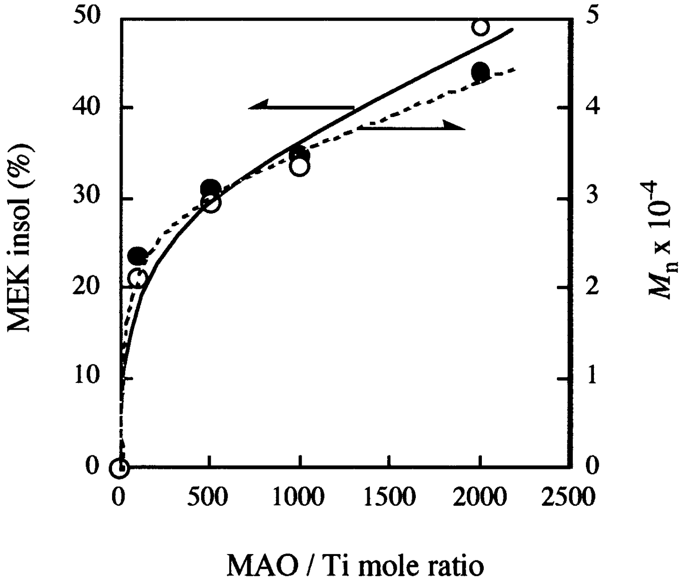


Figure 2. The effects of the MAO / Ti mole ratio on the copolymerization of St and SSTM using the $CpTiCl_3$ / MAO catalyst; [St] = 2.9 mol/L, [Ti] = 4.7 x 10^{-4} mol/L, [SSTM]; *M*n = 1100.

Conclusion

Form the polymerization behavior of the copolymerization of St with the SSTM using the $CpTiCl_3$/MAO catalyst, it was indicated that the polymerization reactivities using the SSTM were different from the copolymerization with the SIPM. The miscibility between the main chain and the side chain caused a different copolymerization behavior. We presumed that the difference in the incorporated macromonomers in the graft copolymer was attributed to the miscibility between the syndiotactic main chain and the side chain.

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