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Synthesis of star polymer by means of the living polymerization of [(*o*-trifluoromethyl)phenyl]acetylene using a $MoOCl_4$-based catalyst and the linking method

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Abstract

A star polymer was synthesized by addition of 1,4-diethynyl-2,5-dimethylbenzene as linking agent (30 °C, 24 h) after living polymerization of [(*o*-trifluoromethyl)phenyl]acetylene (*o*-CF_3PA) with $MoOCl_4$–*n*-Bu_4Sn–EtOH catalyst (in anisole, 30 °C, 20 min; [Mo] = 10 mM, [P*]/[Mo] = 40%, [*o*-CF_3PA]$_0$ = 200 mM). The M_n values of the living and star polymers were 8.1×10^3 and 5.3×10^4, respectively, according to gel permeation chromatography, while these values determined by multi-angle laser light scattering (MALLS) were 7.8×10^3 and 2.5×10^5. The M_w/M_n and arm number of the star polymer were 1.04 and 29, respectively, according to MALLS. The molecular weight and arm number of star polymer increased with increasing linking agent concentration and polymerization temperature.

Keywords: Substituted polyacetylene; Living polymerization; Star polymer

1. Introduction

Star polymers are the three-dimensional polymers that consist of a number of linear polymeric chains (arms) attached to a relatively small central moiety (core) [1]. These polymers are expected to have different properties from linear polymers owing to their sterically small size, spherical structure, and small interaction between molecules. They are usually prepared by one of the following methods: (1) a monomer is polymerized with a multifunctional initiating agent; (2) a linear living polymer is terminated with a multi-functional terminator; and (3) a linear living polymer is linked to one another with a linking agent (e.g. divinyl compounds). A feature of method (3) is that star polymers with many arms can be synthesized, although it is difficult to control the arm number.

Kanaoka et al. have synthesized star polymers [2–5] from vinyl monomers by applying method (3) to living cationic polymerization. The synthesis of star polymers based on controlled radical polymerization and method (3) have been reported by Baek et al. [6,7]. Further, concerning the star polymer with conjugated polymer arms, star polymers with substituted polythiophene arms have been reported by Wang et al. [8–10]. However, there has been no report about star polymers from substituted acetylene monomers.

As substituted polyacetylenes have the alternating double bond structure along the main chain, the star polymers based on them are expected to display novel properties. We have reported that the $MoOCl_4$–*n*-Bu_4Sn–EtOH system [11] serves as living polymerization catalyst for a number of substituted acetylenes such as *ortho*-substituted phenylacetylenes [12,13], 1-chloro-1-alkynes [14], 1-chloro-2-phenylacetylene [15], *t*-butylacetylene [16], and linear internal alkynes [17].

In the present study, we report the synthesis of a novel star polymer from a substituted acetylene by means of method (3). [(*o*-Trifluoromethyl)phenyl]acetylene (*o*-CF_3PA) was used as monomer because it shows an excellent living nature in the polymerization catalyzed by $MoOCl_4$–*n*-Bu_4Sn–EtOH. 1,4-Diethynylbenzene (DEB) and 1,4-diethynyl-2,5-dimethylbenzene (DEDMB) were employed as linking agents (Chart 1). DEDMB, which has a methyl group at the *ortho* position to the ethynyl groups, proved to

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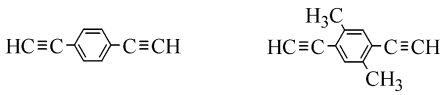


DEB DEDMB

Chart 1.

be very effective as linking agent. The reaction scheme is shown in Scheme 1.

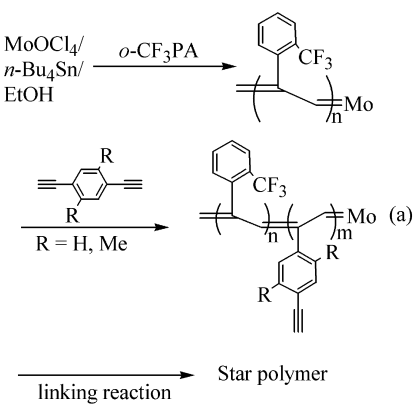
2. Experimental

2.1. Materials

o-CF_3PA was prepared as described in literature [18,19] and distilled twice from CaH_2 at reduced pressure before use. DEB and DEDMB, which were used as linking agents, were prepared according to the literature methods [20] and purified by flash column chromatography (Nakalai Tesque Co., silica gel 60; eluent: hexane). $MoOCl_4$ (Strem) was commercially obtained and used without further purification. Anisole as polymerization solvent was washed with aqueous sodium hydroxide solution (5%) and water successively, dried over anhydrous calcium chloride, and distilled twice from sodium metal [purity > 99.9% (GC)]. *n*-Bu_4Sn as cocatalyst and EtOH as third catalyst component were distilled and stored as anisole solution.

2.2. Polymerization

All the procedures were carried out under dry nitrogen in a pre-baked Schlenk tube equipped with a three-way stopcock. Catalyst solutions were prepared as follows: an anisole solution of $MoOCl_4$ and an anisole solution of *n*-Bu_4Sn were mixed, and the mixture was aged at room temperature for 15 min. An anisole solution of EtOH was further added to the $MoOCl_4$–*n*-Bu_4Sn solution, and the mixture was aged at room temperature for an additional 15 min. Polymerization was started by addition of *o*-CF_3PA to the mixture. After polymerization for 20 min, *o*-CF_3PA was completely consumed to give a living polymer, and then a linking agent was added to the polymerization system. Polymerization was quenched usually after 24 h by addition of EtOH. The conversions of *o*-CF_3PA and linking agent were determined by GC. The formed polymers were isolated by precipitation in hexane and dried in vacuo.



Scheme 1.

2.3. Characterization

The molecular weight distributions of polymers were recorded by gel permeation chromatography (GPC) (Jasco PU930; eluent: chloroform; Shodex K805, 804, 803 polystyrene gel columns; RI detector). The number- and weight-average molecular weights (M_n and M_w, respectively) of polymers were determined by using a polystyrene calibration. Initiation efficiencies ([P^*]/[Cat]) were calculated from the polymer yield and the degree of polymerization (DP) of polymer. Further, the M_n and M_w values of a few polymers were also determined by multi-angle laser light scattering (MALLS). The MALLS measurements were performed in $CHCl_3$ at 40 °C on a Dawn E instrument (Wyatt Technology; Ga–As laser, $\lambda = 690$ nm). The refractive index increment (d*n*/d*c*) was measured in $CHCl_3$ at 25 °C on a Photal DRM-1020 refractmeter ($\lambda =$ 633 nm). The d*n*/d*c* value of the star polymer was 0.174 ml/g.

3. Results and discussion

DEB was used as linking agent and effect of DEB concentration was examined (Fig. 1). The linear living polymer ($M_n = 8100$ by GPC) was at first prepared by polymerization in anisole at 30 °C for 15 min. When DEB was added to the living polymer ($r =$ [DEB]/[P^*] = 5), the conversion of DEB was 100% after 24 h according to GC, and the linear living polymer was almost completely linked,

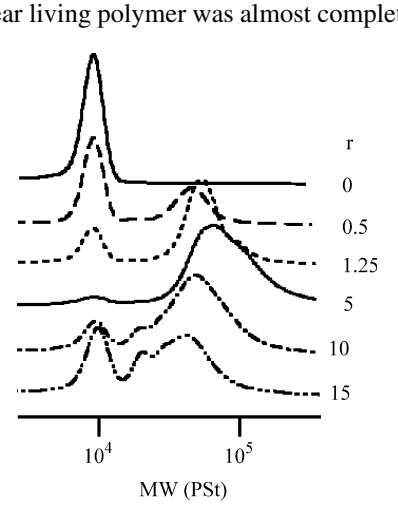


Fig. 1. Effect of [DEB] on the GPC profile of star poly(*o*-CF_3PA) (polymerized in anisole, 30 °C, 15 min; [$MoOCl_4$] = 10 mM, [*o*-CF_3PA] = 200 mM, [P^*]/[$MoOCl_4$] = 40%. Linking reaction 30 °C, 24 h; $r =$ [DEB]/[P^*]. The conversions of DEB were 100% ($r = 0.5$, 1.25, 5) and ~95% ($r = 10$, 15)).

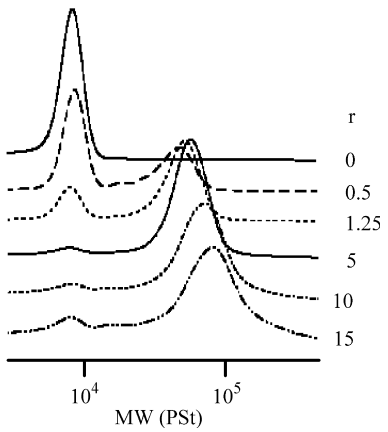


Fig. 2. Effect of [DEDMB] on the GPC profile of star poly(*o*-CF_3PA) (polymerized in anisole, 30 °C, 15 min; [$MoOCl_4$] = 10 mM, [*o*-CF_3PA] = 200 mM, [P^*]/[$MoOCl_4$] = 40%. Linking reaction 30 °C, 24 h; r = [DEDMB]/[P^*]. All the conversions of DEDMB were 100%).

as is seen from a unimodal peak of star polymer in a higher molecular weight region in the GPC curve. However, when r was smaller (0.5, 1.25), the linear living polymer was not completely linked and partly remained unreacted. As r was appreciably increased (10, 15), the molecular weight of star polymer decreased and the GPC shows a multi-modal profile. This is probably because the propagating end having DEB was gradually inactivated before complete linking reaction (Scheme 1(a)), as is presumed from the fact that phenylacetylene does not polymerize in a living fashion with this $MoOCl_4$-based catalyst.

In order that a linking agent is highly efficient, it should react in a living fashion. It is known that (*o*-methylphenyl) acetylene polymerizes in a living manner with $MoOCl_4$-based catalysts, whereas phenylacetylene does not [12,13]. Thus, DEDMB was next examined as linking agent (Fig. 2). DEDMB was completely consumed at all the r([DEDMB]/[P^*]) values examined. When the r value was 0.5 and 1.25, 58 and 22% of the linear polymer remained, respectively, whereas almost no linear polymer was observed in GPC curves when r was 5 or larger. A unimodal peak of the

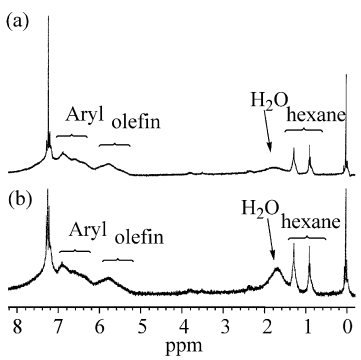


Fig. 3. ^{1}H NMR (in $CDCl_3$) spectra of linear poly(*o*-CF_3PA) (a) and star poly(*o*-CF_3PA) (b). Polymerized in anisole at 30 °C for 15 min; [$MoOCl_4$] = 10 mM, [*o*-CF_3PA] = 200 mM, [P^*]/[$MoOCl_4$] = 40%. Linking reaction carried out at 30 °C for 24 h; [DEDMB]/[P^*] = 5; the conversion of DEDMB was 100%.

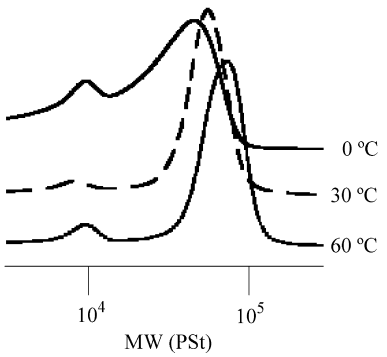


Fig. 5. Effect of linking temperature on the GPC profile of star poly(*o*-CF_3PA) (polymerized in anisole, 30 °C, 15 min; [$MoOCl_4$] = 10 mM, [*o*-CF_3PA] = 200 mM, [P^*]/[$MoOCl_4$] = 40%. Linking reaction 24 h; r = [DEDMB]/[P^*] = 5. All the conversions of DEDMB were 100%).

formed star polymer shifted to higher molecular weight regions with increasing r. This indicates that DEDMB polymerizes in a living fashion and is very effective as linking agent. The formed star polymer was soluble in toluene, THF and $CHCl_3$, but insoluble in hexane, acetone, DMF and methanol.

The ^{1}H NMR spectrum of the linear polymer showed a broad peak around $\delta = 5.8$ *ppm*, which is assigned to the olefinic proton of the main chain with *cis* structure (Fig. 3(a), in $CDCl_3$). The ^{1}H NMR spectrum of the star polymer was similar to that of the linear polymer (Fig. 3(b)). The peak of the methyl proton of the linking agent was not observed, which is attributed to the lower mobility of the core and, in turn, the corresponding large variations of the relaxation times in NMR, which agrees with the result that the star polymer has been formed.

Time dependence of the linking reaction was examined (Fig. 4). After 2 min, DEDMB was completely consumed and about 75% of the linear polymer was consumed to give a star polymer. With reaction times of 30 min to 2 h, the linear polymer was almost completely linked. No further

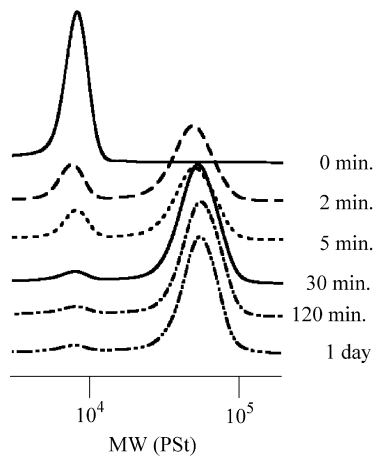


Fig. 4. Effect of linking time on the GPC profile of star poly(*o*-CF_3PA) (polymerized in anisole, 30 °C, 15 min; [$MoOCl_4$] = 10 mM, [*o*-CF_3PA] = 200 mM, [P^*]/[$MoOCl_4$] = 40%. Linking reaction 30 °C; r = [DEDMB]/[P^*] = 5. All the conversions of DEDMB were 100%).

Table 1
Effect of DP of linear living polymer on the synthesis of star polymer from *o*-CF_3PA and DEDMB

Linear living polymer (arm)				Star polymer				
$[o\text{-}CF_3PA]_0$ (mM)	$M_n/10^3$		DP[a]	$M_n/10^3$		M_w/M_n	f[b]	
	GPC	MALLS		GPC	MALLS		GPC	MALLS
50	1.7	1.5	9	38	8800	Very broad	16	4300
100	4.2	3.9	23	31	330	1.12	6	72
200	8.1	7.8	46	53	250	1.04	6	29

Polymerized in anisole at 30 °C for 1 day; $[MoOCl_4] = 10$ mM, $[P^*]/[MoOCl_4] = 40\%$. Linking reaction: 30 °C, 24 h; $r = [DEDMB]/[P^*] = 5$.
[a] Determined by MALLS.
[b] The number of arms: $f = M_n$(star) × (weight fraction of *o*-CF_3PA in star-shaped polymer)/M_n(linear).

change of peak pattern was seen in the GPC curve even after 1 day, which indicates that coupling reaction between the formed star polymers did not occur. Therefore, one can select the linking time in a wide range of 30 min to 2 h.

The effect of temperature on the linking reaction was investigated (Fig. 5). The temperature was changed from 30 to 0 °C or 60 °C. Consequently, the molecular weight of polymer increased with increasing temperature from 0 to 60 °C, and the extent of linking reaction was virtually quantitative at 30 and 60 °C. It is supposed that the linking reaction is accelerated and proceeds to completion at such high temperatures.

Table 1 shows the effect of the DP of living polymer (arm). Molecular weights were measured by both GPC and MALLS. The M_n values of the linear polymers determined by GPC and MALLS essentially coincided with each other. On the other hand, the M_n values of the star polymers determined by MALLS were much larger than the counterparts based on GPC. This is reasonable because star polymers have more compact structure than the linear polymers with the same molecular weight. When the arm length was made larger, the arm number decreased, and, in turn, the M_n of star polymer also decreased. This indicates that a longer arm causes a larger steric hindrance in linking reaction. When the DP of linear polymer was as small as 9, the M_n of star polymer became very large and the GPC peak was very broad. This is attributed to the linking reaction between star polymers. In the case that the DPs of linear polymers were 23 and 46, the M_w/M_n values determined by MALLS were about 1.1, indicating narrow MWD. Further, it is noted that the arm numbers of these star polymers are 72 and 29 and appreciably large.

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References

[1] For reviews on the properties of star polymer, see: Roovers J. Star hyperbranched polymers. New York: Marcel Dekker; 1999. p. 285. Marsalko TM, Majoros I, Kennedy JP. Pure Appl Chem 1997;A34: 775. Bywater S. Adv Polym Sci 1979;30:90. Bauer BJ, Fetters LJ. Rubber Chem Technol 1978;51:406.
[2] Kanaoka S, Sawamoto M, Higashimura T. Macromolecules 1991;24: 2309.
[3] Kanaoka S, Sawamoto M, Higashimura T. Macromolecules 1991;24: 5741.
[4] Kanaoka S, Sawamoto M, Higashimura T. Makromol Chem 1993; 194(7):2035.
[5] Kanaoka S, Omura T, Sawamoto M, Higashimura T. Macromolecules 1992;25:6407.
[6] Baek KY, Kamigaito M, Sawamoto M. Macromolecules 2001;34:215.
[7] Baek KY, Kamigaito M, Sawamoto M. J Polym Sci Part A: Polym Chem 2002;40:633.
[8] Wang F, Rauh RD, Rose TL. J Am Chem Soc 1997;119:11106.
[9] Wang F, Wilson MS, Rauh RD, Schottland P, Reynolds JR. Macromolecules 1999;32:4272.
[10] Wang F, Wilson MS, Rauh RD, Schottland P, Thompson BC, Reynolds JR. Macromolecules 2000;33:2083.
[11] Hayano S, Masuda T, Iwawaki E, Nomura R. J Mol Catal A: Chem 1998;133:213.
[12] Mizumoto T, Masuda T, Higashimura T. Macromol Chem Phys 1995; 196:1769.
[13] Kaneshiro H, Masuda T, Higashimura T. Polym Bull 1995;35:17.
[14] Masuda T, Yoshimura T, Higashimura T. Macromolecules 1989;22: 3804.
[15] Hayano S, Masuda T. J Macromol Sci: Pure Appl Chem 2000;A37(8): 853.
[16] Nakano M, Masuda T, Higashimura T. Macromolecules 1994;27: 1344.
[17] Kubo H, Hayano S, Masuda T. J Polym Sci Part A: Polym Chem 2000;38:2697.
[18] Brandsma L, Hommes H, de Jong RLP, Verkruijsse HD. Recl Trav Chim Pays-Bas 1985;104:226.
[19] Sonogashira K, Tohda Y, Hagihara N. Tetrahedron Lett 1975;50: 4467.
[20] Takahashi S, Kuroyama Y, Sonogashira K, Hagihara N. Synth Commun 1980;627.