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Synthesis and Properties of Cross-Linked Poly(vinylene-arsine)

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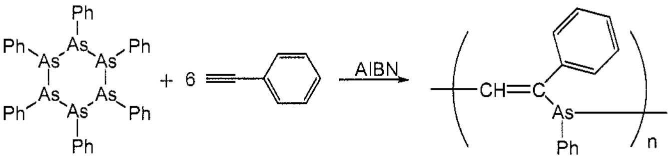
Summary

Cross-linked poly(vinylene-arsine)s (**4**) were synthesized by a free-radical terpolymerization of phenylacetylene (**2**), hexaphenylcyclohexaarsine (**1**), and *p*- or *m*-diethynylbenzene (*p*- or *m*-**3**) at different compositions in the presence of a catalytic amount of AIBN. The number-average molecular weights of the resulting polymers were a few thousands estimated by gel permeation chromatography (GPC) analysis. By gas chromatography (GC) analysis *p*-**3** was found to be more reactive during the polymerization than *m*-**3** and the resulting cross-linked polymer (*p*-**4**) showed lower solubility than that of *m*-**4**. The cross-linked poly(vinylene-arsine)s showed higher glass transition temperature in the measurement of differential scanning calorimetry (DSC) and more red-shifted emission in chloroform solution than that of the linear poly(vinylene-arsine). These properties could be tuned by varying the monomer feed ratio.

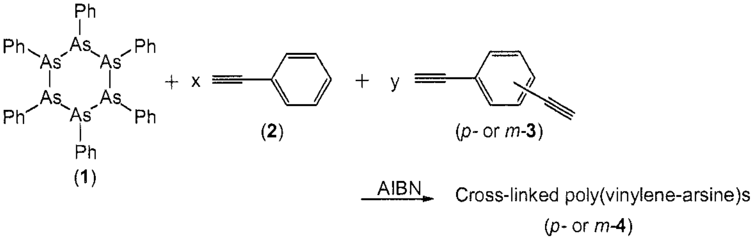
Introduction

Organic / inorganic hybrid polymers, i. e., macromolecules where inorganic elements play the key role in the backbone, possess characteristic properties which are different from "organic polymers" with backbones consisted of either only carbon or carbon in combination with oxygen or nitrogen [1-4]. Recently, as a part of our sequential research on the development of the synthetic methodology and the properties of the novel heteroatom-containing polymers [5-10], we reported the ring-collapsed radical alternating copolymerization of arsenic homocyclic compounds with acetylenic compounds using 2,2'-azobisisobutyronitrile (AIBN) as a radical initiator [11-12] to produce the corresponding alternating copolymer, poly(vinylene-arsine) (Scheme 1). The obtained polymer is the first example of the soluble polymer having arsenic atoms in the main chain with a well-defined structure. Regardless of the feed ratio of two monomers, the copolymerization produced the polymer with 1 : 1 alternating structure of arsenic unit and vinylbenzene unit in the backbone. The extension of the conjugation length via lone pair on the arsenic atoms in the polymer chain was proved by the UV-vis absorption spectrum. The alternating copolymer showed fluorescent properties attributable to the n-π* transition in the backbone [12]. Besides the optical properties, the poly(vinylene-arsine)s can have many functionalities, for example, to form a polymer complex with a various kinds of transition metals and to act as a reducing agent due to the lone pair on the arsenic atom.



Scheme 1. Synthesis of linear poly(vinylene-arsine).

On the other hand, conjugated cross-linked polymer networks (gels) have been studied owing to the unique properties, such as environmental responses [13] and enhanced conductivities [14-15]. In this article, we describe the synthesis of cross-linked poly(vinylene-arsine)s by the radical terpolymerization of cyclooligoarsine, phenylacetylene, and *p*- or *m*-diethynylbenzene (Scheme 2). If each polymer chain with the structure of vinylene-arsine is cross-linked by one another, the electrical structure would be affected due to the enhancement of the interchain interaction, and thus more extension of the conjugation length would be expected. In addition, closely packed structure might improve the thermal stability of the poly(vinylene-arsine)s.



Scheme 2. Synthesis of cross-linked poly(vinylene-arsine).

Experimental

Materials

Unless otherwise noted, all reagents and chemicals were purchased from Wako Pure Chemical Industries, Ltd. Toluene (water < 30 ppm) was bubbled with a stream of nitrogen before use. *n*-Hexane (water < 30 ppm), methanol (water < 50 ppm), and *n*-dodecane were used without further purification. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Phenylacetylene (**2**) was purchased from Aldrich and purified by the distillation under reduced pressure. *p*-Diethynylbenzene (*p*-**3**) was obtained from Tokyo Kasei, Inc. and sublimed under reduced pressure. *m*-Diethynylbenzene (*m*-**3**) was used as received from Tokyo Kasei, Inc. Hexaphenylhexacycloarsine (**1**) was synthesized using a literature procedure [16].

Instruments

All reactions were carried out under an atmosphere of prepurified nitrogen using Schlenk techniques. ^1H and ^{13}C NMR spectra were obtained using a JEOL JNM-EX270 instrument (270 and 67.5 MHz, respectively) for solutions in $CDCl_3$ and were referenced to $SiMe_4$ (TMS). Gel permeation chromatographic (GPC) analyses were carried out on a Tosoh 8020 instrument with a TSH-gel Alpha 3000 column with DMF solution containing 10mM LiBr as an eluent after calibration with polystyrene standards. Gas chromatography (GC) analyses were carried out on a SHIMADZU GC-17A using helium gas as a carrier gas. UV-vis spectra were measured on a JASCO V-530 spectrometer with the samples being analyzed in $CHCl_3$ at room temperature. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer with the samples being analyzed in $CHCl_3$ at room temperature. Differential scanning calorimetry (DSC) thermograms were obtained with a DSC200, Seiko Instruments Inc., with the heating rate of 10 $^oCmin^{-1}$ under nitrogen atmosphere.

Synthesis of cross-linked poly(vinylene-arsine)s

A typical experimental procedure is as follows. Under a nitrogen atmosphere, a benzene solution (0.5 mL) of AIBN (0.009 g, 0.05 mmol) was added to a refluxing solution of phenylacetylene (**2**) (0.1 g, 0.9 mmol), hexaphenylhexacycloarsine (**1**) (0.27 g, 0.30 mmol), and *p*-diethynylbenzene (*p*-**3**) (0.06 g, 0.45 mmol) in benzene (4.5 mL). After being stirred for 12 h, *n*-hexane was poured into the reaction mixture to precipitate the product, which was then purified three times by reprecipitation from benzene to *n*-hexane. After freeze-drying for 10 h, the corresponding cross-linked polymer (*p*-**4**) was obtained as a yellow powder (0.23 g) in 51% yield. ^1H NMR ($CDCl_3$, ppm): 5.8 – 8.2 (C=CH, ArH); ^{13}C NMR ($CDCl_3$, ppm): 126–128, 129-131 ($C_{Ar}H$), 131–133 (*C*H=C), 134-135 (*C*-C_{Ar}, C_{Ar}-As), 136-144 (CH=*C*).

GC analysis of the reaction mixture during the terpolymerization

The radical terpolymerization of **1**, **2**, and **3** using AIBN in the same feed ratio as above was in the presence of *n*-dodecane (0.10 mL) as a standard material. The moment of the addition of a benzene solution of AIBN was defined as the start time of the copolymerization. During the polymerization, a small amount of the reaction mixture was siphoned, dilute with benzene, and analyzed by GC. The consumption rates of **2** and **3** were calculated from the peak area ratios of **2** and **3** with *n*-dodecane.

Results and discussion

Synthesis of cross-linked poly(vinylene-arsine)

A typical terpolymerization procedure (Run 3 in Table 1) of hexaphenylcyclohexaarsine (**1**), phenylacetylene (**2**), and *p*- or *m*-diethynylbenzene (**3**) was conducted as follows. Under a nitrogen atmosphere, a mixture of **1**, **2**, *p*-**3**, and AIBN at a feed ratio of 1 : 3 : 1.5 : 0.17 was stirred in refluxing benzene for 12 hours. In this monomer feed ratio, the molar ratio of the phenylarsine unit (PhAs) with total ethynyl group was unity. In the early stage of the polymerization, the reaction mixture was heterogeneous due to the insolubility of **1** in benzene. Within about 30 minutes after the initiation of the polymerization, the reaction mixture became homogeneous, suggesting that the ring structure of **1** collapsed completely. The reaction mixture maintained the homogeneity until the polymerization was ceased. After stirring, the reaction mixture was poured into *n*-hexane to precipitate the polymeric material. The resulting polymer was purified by reprecipitation from benzene to *n*-hexane three times, and freeze-dried for 10 h to yield the corresponding cross-linked poly(vinylene-arsine) as a yellow powder in 51 %. The relatively low yield of the isolated polymer was due to the removal of low molecular weight products by the reprecipitation. The obtained polymer was soluble in common organic solvents such as benzene, toluene, chloroform, and DMF and showed a single peak on the GPC (DMF as a solvent) trace. The number-average molecular weight was estimated by the GPC analysis and found to be 2 800 (*vs* polystyrene standards) with the polydispersity index (PDI) of 4.2. The higher value of PDI of the resulting polymer than that of the linear poly(vinylene-arsine) (Run 1 in Table 1) suggests the cross-linked polymer structure. ^{1}H NMR and ^{13}C NMR spectra of the obtained polymer supported the polymer structure of vinylene-arsine. The absence of an obvious peak around 3 ppm in the ^{1}H NMR spectrum indicates that the cross-linked polymer possesses no residue of ethynyl groups.

Table 1. Results of copolymerization

Run	**3**	Feed Ratio **2** / **3**	M_w[a]	M_n[a]	M_w/M_n[a]	Yield (%)[b]	Solubility[c]	T_g[d] (°C)
1		6.0 / 0	3100	1700	1.8	27	soluble	92.9
2	*p*-	5.0 / 0.5	3700	1900	1.9	29	soluble	92.9
3	*p*-	3.0 / 1.5	11800	2800	4.2	51	soluble[e]	101.7
4	*p*-	2.0 / 2.0	ND[f]	ND	ND	62	insoluble	104.9
5	*m*-	3.0 / 1.5	7800	2700	2.9	48	soluble	99.2
6	*m*-	2.0 / 2.0	8000	2600	3.1	54	soluble	103.7

[a] Determined by GPC analysis (DMF, polystyrene standards). [b] Isolated yields after reprecipitation into n-hexane. [c] Solubility of 250 mg of the polymer in 5.0 mL of benzene, chloroform, and DMF. [d] Determined by DSC measurement. [e] Decreased solubility in benzene. [f] ND = not determined.

Terpolymerization in the various monomer feed ratio and properties of the cross-linked polymers

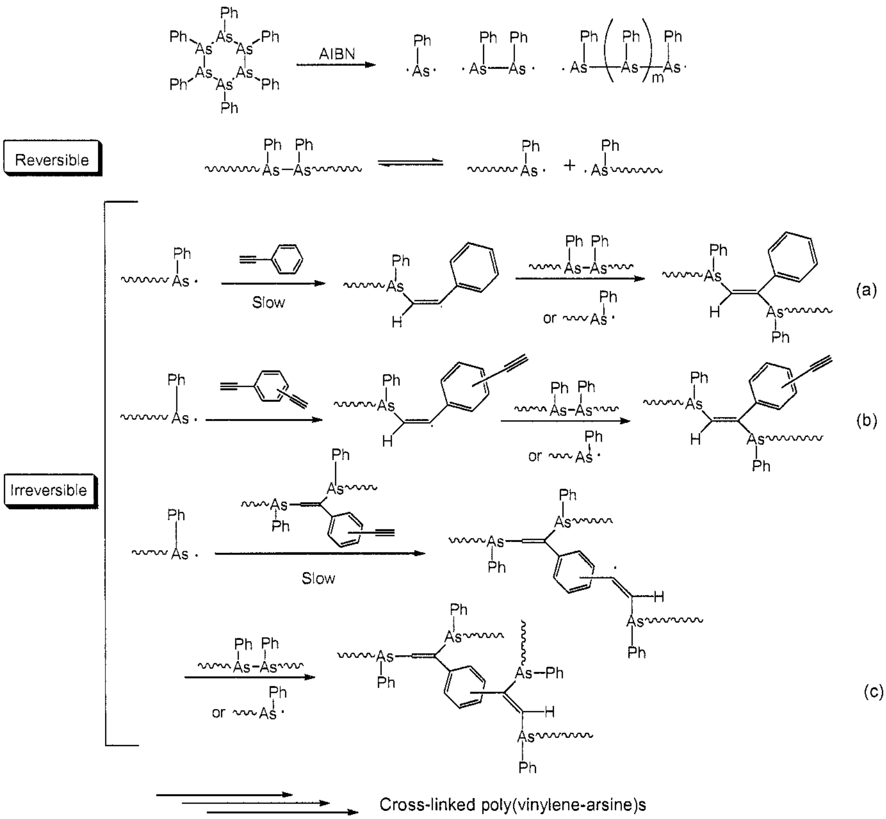
We carried out the terpolymerizations at different compositions of **1**, **2**, and *p*- or *m*-**3** with a catalytic amount of AIBN in refluxing benzene to investigate their effects in the polymerization behavior and the polymer properties. The monomer feed ratios, the molecular weights, yields, and solubility of the obtained polymers were summarized in Table 1. In all cases the same molar amount of the PhAs unit as that of total ethynyl group was employed. In Run 4 where we employed **2** and *p*-**3** with a molar ratio of 1 : 1, the reaction mixture became heterogeneous due to the deposition of the insoluble polymeric material within 2 h after the terpolymerization was initiated. The GPC analyses showed that the polydispersity index (PDI) of the polymers increased with the concentration of the diethynylbenzene in the terpolymerization. This result suggests that the diethynylbenzenes acted as a cross-linking agent and cross-linking points in the polymer increased with the feed ratio of diethynylbenzene. All of the copolymers except that of Run 4 were soluble in common organic solvents (Table 1). Apparently, the copolymers from *p*-**3** are of lower solubilities than those from *m*-**3**, indicating that the copolymers from *p*-**3** possess more cross-linking point than those from *m*-**3**. All of the polymers except for that of Run 4 were analyzed by ^{1}H and ^{13}C NMR spectroscopies and their main-chain structures of vinylene-arsine were supported. Though the polymer obtained in Run 4 was insoluble and difficult to be characterized, it must be the cross-linked poly(vinylene-arsine) as well as others. Since the polymer in Run 4 possessed more cross-linking point than others, it showed a lower solubility and deposit during the terpolymerization.

We made polymer films by letting a few drops of the polymer solutions except for that of Run 4 in chloroform(250 mg of the polymer in 5.0 mL of chloroform) stand dried on the slip glasses at room temperature. All the terpolymers exhibited a film-forming property. We compared the degree of the difficulty of the films to be peeled off the slip glasses, and found to increase in the following order: polymer film of Run 1 $\approx$ of Run 2 $<$ of Run 3 and of Run 5 $<$ of Run 6. The same order is observed for increasing concentration of diethynylbenzene in the copolymerization. Thus, incorporating diethynylbenzene in the copolymerization yields polymers which exhibit improved film-forming property. The polymers with the more cross-linking point possess the larger weight-average molecular weight, and hence the more improved processability.

Terpolymerization mechanism

The mechanism of the present terpolymerization should be the same as that of the linear copolymers except that diethynylbenzene participates in the rate-determining step in the polymerization (Scheme 3) [11]. First, AIBN cleaved the arsenic-arsenic bond of **1** to produce arsenic radicals. Second, the homolysis of the other arsenic-arsenic bonds proceeded spontaneously due to their instability by the destruction of the quite stable six-membered-ring structure. In competition with this reaction, the arsenic radical added to **2** (path (a)), *p*-or *m*-**3** (path (b)), or the ethynyl group at the polymer side chain (path (c)) to give a vinyl radical. Due to the instability of the produced vinyl radical, this addition is the rate-determining step of this polymerization. Next the vinyl radical reacted immediately with the arsenic-arsenic bond or with the arsenic radical to form a new carbon-arsenic bond.

The radical terpolymerization of **1**, **2**, and *p*- or *m*-**3** in the feed ratio of 1 : 3.0 : 1.5 was carried out in the presence of *n*-dodecane as a reference material to monitor the amount of consumption of the monomers **2** and *p*- or *m*-**3** by using gas chromatography (GC) analysis. All of the experiments were performed three times, and the average values are presented with error bars in Figure 1. In both cases the diethynylbenzenes (*p*- and *m*-**3**) were consumed much faster than phenylacetylene. When comparing *p*- and *m*-**3**, it is the former that is more reactive than the latter. The difference in the reactivity between *p*- and *m*-diethynylbenzene was obvious during the first hour of the reaction, reaching as high as 30 % after 15 minutes since the reaction started. We already studied and reported that the reactivity of acetylenic compounds with the arsenic radical becomes higher when the acetylenic monomer bore a conjugated substitution [12]. The unstable vinyl radical was stabilized by the resonance effect and thus the formation of it (rate-determining step) was promoted. The resonance stabilization acts much more effectively with a *p*-conjugated substitution than a *m*-substitution. Therefore the consumption of *p*-**3** was faster than that of *m*-**3** and, in addition, than two times of the consumption rate of **2**. Although ^{1}H NMR of all the cross-linked polymers except that of Run 4 showed no peaks assigned to acetylenic protons, the reactivity of the residue ethynyl group at the side chain of the polymer from *p*-**3** should be higher than that from *m*-**3** due to the more efficient resonance effect or steric effect. Therefore, *p*-**3** acts as a more effective cross-linker than *m*-**3** during the terpolymerization. The final conversion ratio of **2** with *p*- or *m*-**3** (Figure 1) revealed that the ratio of diethynylbenzene unit in the polymer structure is higher in the polymer from *p*-**3** than that from *m*-*3*.



Scheme 3. Mechanism of the terpolymerization.

Thermal and optical properties of the cross-linked poly(vinylene-arsine)

To investigate the thermal properties of the obtained cross-linked polymers, the DSC analyses were carried out under nitrogen atmosphere. The values of glass transition

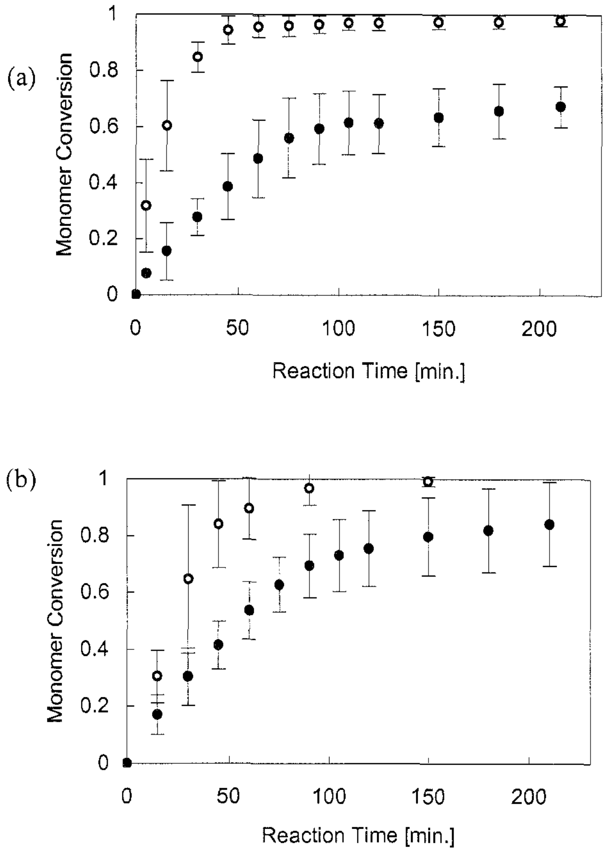


Figure 1. Time-conversion plot of (a) **2** (●) and *p*-**3** (○) and (b) **2** (●) and *m*-**3** (○) during the terpolymerization with **1** in the feed ratio of **1** : **2** : *p*- or *m*-**3** = 1 : 3 : 1.5.

temperatures (T_g) are listed in Table 1. As expected, the T_g value increases with the content of the cross-linker, diethynylbenzene, and when the feed ratio of the *p*- and *m*-**3** was same (Table 1, Run 2 *vs* Run 5 and Run 3 *vs* Run 6) the polymers from *p*-**3** showed higher T_g than those from *m*-**3**. This might due to increase weight average molecular weights of the cross-linked polymers by increase efficiency of the cross-linking agents. All of the resulting polymers were stable in the solid state at room temperature. No decrease of the molecular weight or no change of the structure was observed even after exposing them to air for several months.

In the UV-vis spectra measured in dilute chloroform solutions, the cross-linked polymers exhibited not only strong absorption in the UV region derived from a π–π* transition of C=C but also small absorption in the visible region as observed in that of the linear poly(vinylene-arsine). The lower energy absorption was attributable to a delocalized n–π* transition in the backbone of the polymer [12]. The absorption edges of the obtained polymers were located around 500 nm.

The fluorescent emission spectrum of the polymer in Run 3 (Figure 2; in chloroform at room temperature; excitation wavelength at 394 nm) showed an emission in the blue region with a peak at 473 nm. The location of the emission and excitation peak maxima summarized in Table 2 Run 2-6. Those peaks of the cross-linked polymers were red-shifted compared to those of linear poly(vinylene-arsine) (Table 2, Run 1). The favorable interchain interaction of the poly(vinylene-arsine) moiety by the cross-linker and the extension of the effective conjugation length through the conjugated cross-linking bond resulted in the narrower band gap. The longer extension of the conjugation path by *p*-substituted cross-linker than by *m*-substituted one (Table 2, Run 3 *vs* Run 5 and Run 4 *vs* Run 6) might be derived from the more efficient resonance effect of the conjugated *p*-substitution.

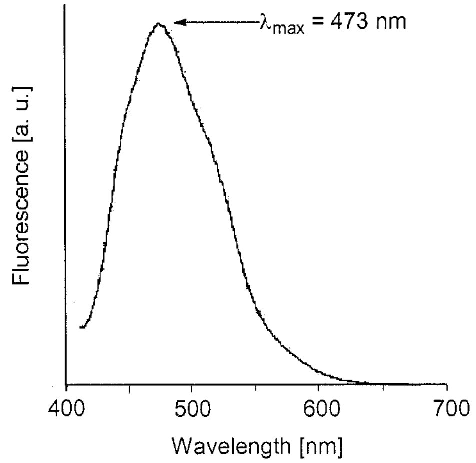


Figure 2. Fluorescence spectrum of the polymer of Run 3 excited at 394 nm recorded in chloroform at 25 °C.

Table 2. Emission and excitation peak maxima.

Run[a]	**3**	Feed Ratio **2** / **3**	Emission λ_{max} / nm (Excitation wavelength / nm)	Excitation λ_{max} / nm (Emission wavelength / nm)
1		6.0 / 0	437	375
2	*p*-	5.0 / 0.5	470	392
3	*p*-	3.0 / 1.5	473	394
4	*p*-	2.0 / 2.0	ND[b]	ND
5	*m*-	3.0 / 1.5	465	392
6	*m*-	2.0 / 2.0	464	391

[a] Measured in chloroform at 25 °C. [b] ND = not determined.

Conclusion

We have verified in this research that incorporating *p*- or *m*-diethynylbenzene as a cross-linking agent in the radical polymerization of phenylacetylene and hexaphenylhexacycloarsine using AIBN as a radical initiator yields cross-linked poly(vinylene-arsine)s. In comparison with the linear poly(vinylene-arsine), the present cross-linked polymers showed more improved film-forming properties, higher glass transition temperatures, and more red-shifted emissions, while the solubilities in organic solvents became lower. These properties can be controlled by varying the monomer feed ratio. The GC analysis revealed that *p*-diethynylbenzene was more reactive than *m*-diethynylbenzene during the terpolymerization due to the higher resonance stabilization of the vinyl radical, and thus acted as more effective cross-linking agent.

References

1. Rehahn M (1998) Acta Polymer. 49: 201.
2. Manners I (1996) Angew. Chem. Int. Ed. Engl. 35: 1602.
3. Nguyen P, Gomez-Elipc P, Manners I (1999) Chem. Rev. 99: 1515.
4. Wright VA, Gates DP, (2002) Angew. Chem. Int. Ed. Engl. 41, 2389.
5. Chujo Y, Tomita I, Hashiguchi Y, Saegusa T (1991) Macromolecules 24: 345.
6. Matsumi N, Naka K, Chujo Y (1998) J. Am. Chem. Soc. 120: 5112.
7. Matsumi N, Umeyama T, Chujo Y (2000) Macromolecules 33: 3956.
8. Naka K, Uemura T, Chujo Y (1998) Macromolecules 31: 7570.
9. Naka K, Uemura T, Chujo Y (2001) J. Am. Chem. Soc. 123: 6209.
10. Morisaki Y, Aiki Y, Chujo Y (2003) Macromolecules 36: 2597.
11. Naka K, Umeyama T, Chujo Y (2002) J. Am. Chem. Soc. 124: 6600.
12. Umeyama T, Naka K, Nakahashi A, Chujo Y, (2004) Macromolecules 37: 1271.
13. Chen L, Kim B-S, Nishino M, Gong JP, Osada Y (2000) Macromolecules 33: 1232.
14. Rebourt E, Pepin-Donat B, Dinh E (1995) Polymer 36: 399.
15. Sixou B, Pepin-Donat B, Nechtschein M (1997) Polymer 38: 1581.
16. Reesor JWB, Wright GF (1957) J. Org. Chem. 22: 382.