Synthesis and properties of copolymers from diphenylacetylene having a hexaphenylbenzene moiety

Masahiro Teraguchi[1], Toshio Masuda[1,*], Andreas Fechtenkötter[2], Klaus Müllen[2]

[1] Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan
[2] Max-Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Summary

Copolymerization of diphenylacetylene having a hexaphenylbenzene group, 1-[*p*-(pentaphenyl)phenyl]-2-phenylacetylene (**1**), with a few other diphenylacetylene derivatives (i.e., diphenylacetylene, 1-phenyl-2-[*p*-(trimethylsilyl)phenyl] acetylene, 1-phenyl-2-[*p*-*n*-octylphenyl]acetylene, (**2a-c**, respectively) and properties of the formed copolymers were investigated. No polymer was obtained in homopolymerization of **1** with $TaCl_5$-*n*-Bu_4Sn catalyst owing to steric hindrance. On the other hand, copolymerization with **2a-c** proceeded at various feed ratios to give copolymers in moderate yields. Copoly(**1/2a**) (feed ratio 25/75) was soluble in toluene and $CHCl_3$ and its weight-average molecular weight (M_w) was ca. 31×10^4 and relatively high. Copoly(**1/2b**) and copoly(**1/2c**) (both feed ratios 5/95) were soluble in common organic solvents, and had a large M_w up to ca. 1×10^6. These copolymers were yellow to orange solids. Oxidative cyclodehydrogenation of hexaphenylbenzene groups in copoly(**1/2a**) was attempted in order to convert them into more conjugated groups.

Introduction

Hexaphenylbenzene can be synthesized in high yield by Diels-Alder reaction of 2,3,4,5-tetraphenylcyclopentadienone with diphenylacetylene, followed by aromatization accompanying under elimination of carbon monoxide. This reaction has been utilized for the polycycloaddition of bis(cyclopentadienone) derivatives with diacetylenes to synthesize various phenyl-substituted poly(phenylenes) (1).

Recently Müllen and coworkers have reported that hexaphenylbenzene derivatives undergoes cyclodehydrogenation under a mild conditions to afford hexa-*peri*-hexabenzocoronene (2). This compound is a fused aromatic ring with highly conjugated structure. Incorporation of the hexa-*peri*-hexabenzocoronene into polymers should give polymers with high carbon content. However, synthesis of polymers containing hexa-*peri*-hexabenzocoronene moieties has hardly been attempted (3).

Substituted polyacetylenes are known as conjugated polymers and have alternating carbon-carbon double bonds along the main chain (4). Among them, poly(diphenylace-tylene) is infusible and insoluble in any solvent. This polymer, however, possesses interesting characteristics. For instance, all the carbons involved are sp^2 carbons, and the polymer is thermally very stable (the onset temperature of weight loss in air (T_0) is ca. 500 °C) (5). On the other hand, diphenylacetylenes with bulky ring substituents give polymers in high yields, which are completely soluble in common organic solvents (6). Interestingly, the formed polymers have extremely high molecular weight ($M_w > 1 \times 10^6$) and can afford tough free-standing films by solution casting. Such properties, i.e.,

---

* Corresponding author

2a: R = H
2b: R = Me₃Si
2c: R = *n*-Oct

1
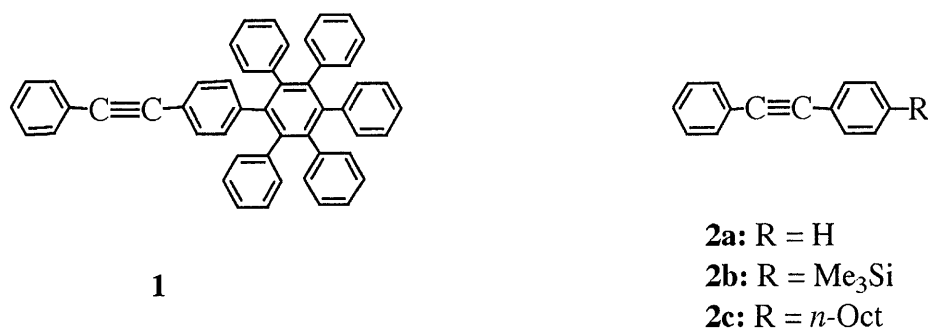
Scheme 1. Monomers used in the present study

solubility, thermal stability and film-forming ability, are important to find practical applications. Recently it has been found that some poly(diphenylacetylene) derivatives show intense electroluminescence and photoluminescence (7).

In this study, copolymerizations of diphenylacetylene having hexaphenylbenzene (**1**) with some diphenylacetylenes and properties of the formed copolymers were investigated. The comonomers used were diphenylacetylene (**2a**), 1-phenyl-2-[*p*-(trimethylsilyl)-phenyl]-acetylene (**2b**), and 1-phenyl-2-(*p*-*n*-octylphenyl) acetylene (**2c**) (Scheme 1). Conversion of the hexaphenylbenzene moiety in copolymer into a more conjugated group was attempted by applying the oxidative cyclodehydrogenation reaction.

Experimental

Materials

n-Bu₄Sn was commercially obtained and distilled twice from CaH₂ before use. TaCl₅ was used as received. **2a** was purchased and purified by sublimation, and **2b** was prepared by the method reported in the literature (6b). **1** and **2c** were synthesized according to Scheme 2 with reference to the literature (3a, 6a).

Synthesis of monomer **1**

(4-Bromophenyl)pentaphenylbenzene, the starting material, was prepared according to reference (3a). Since the corresponding iodide undergoes the following coupling reaction much faster than the bromide, the latter compound was converted into the former (8). Then the coupling reaction of the iodide with phenylacetylene was carried out. The detailed procedures are as follows: A mixture of the bromide (2.7 g, 4.4 mmol), KI (7.8 g, 47 mmol), CuI (4.2 g, 22 mmol), and HMPA (40 mL) was stirred for 6 h at 200 °C under nitrogen. The reaction was monitored by ¹H NMR (the peaks at 6.98 and 6.68 ppm of the bromide diminished and new peaks of the iodide appeared at 7.18 and 6.59 ppm). The reaction mixture was cooled to room temperature and the reaction was quenched by the addition of 2N HCl (100 mL). Subsequently the mixture was poured into benzene (200 mL). The organic phase was washed with water (3x70 mL) and dried over anhydrous Na₂SO₄. Benzene was evaporated to afford pale yellow solid (the crude product was used in the following reaction without further purification). A mixture of the crude iodide (2.5 g), phenylacetylene (0.45 g, 4.4 mmol), (Ph₃P)₂PdCl₂ (31 mg, 0.044 mmol), Ph₃P (47 mg, 0.18 mmol), CuI (50 mg, 0.26 mmol), and Et₃N (0.8 mL, 6.6 mmol) in toluene (50 mL) was stirred under dry nitrogen at 80 °C for 7 h. After the end of the
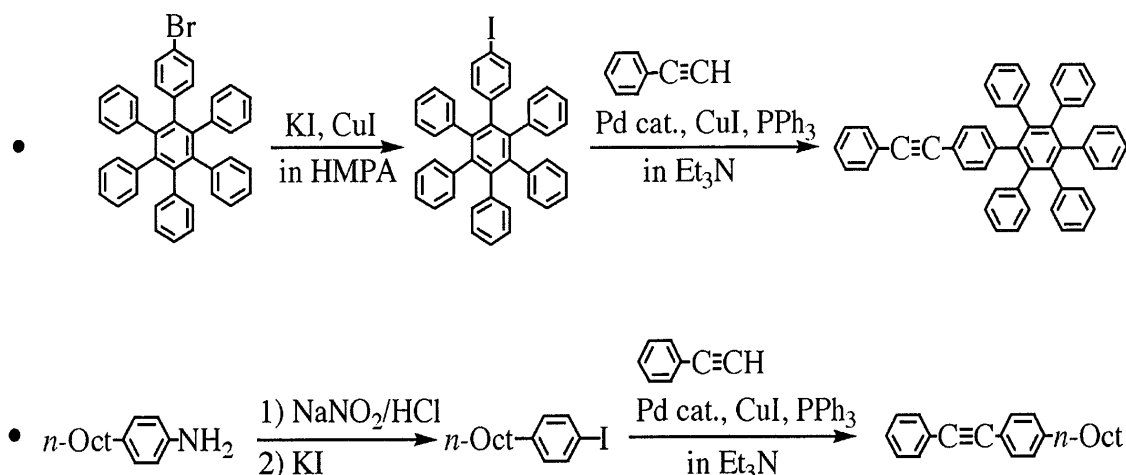
Scheme 2. Monomer synthesis of the present study

reaction had been finished (the completion was confirmed by ^{1}H NMR), the insoluble salt was filtered off and then washed with toluene. The filtrate was washed with 2N HCl and water, and dried over anhydrous Na$_2$SO$_4$. Toluene was evaporated and the crude product was purified by both flash column chromatography (silica gel; eluent: a gradient from hexane/toluene 4/1 to hexane/toluene 1/1) and recrystallization to give a white solid with an overall yield of 43% (based on bromide). IR (KBr) 3083, 3058, 3027, 1945, 1875, 1802, 1750, 1601, 1578, 1509, 1497, 1443, 1399, 1075, 1028, 911, 847, 810, 756, 735, 698, 583, 563, 544 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 7.46-7.40 (m, 2H), 7.33-7.27 (m, 3H), 7.07-7.02 (d, 2H), 6.94-6.80 (m, 27H). ^{13}C NMR (CDCl$_3$) δ 141.08, 140.59, 140.46, 140.40, 140.30, 140.17, 139.56, 131.41, 131.33, 130.00, 128.26, 128.04, 126.76, 126.58, 125.39, 125.23, 123.29, 119.72, 89.78, 88.91.

*Synthesis of monomer **2c***

2c was prepared from 4-*n*-octylaniline as starting material by the same method as for the *n*-Bu homolog reported in reference (6a); colorless oil, overall yield 67%. IR (neat) 3031, 2926, 2855, 2218, 1597, 1512, 1487, 1466, 1443, 1377, 1071, 912, 831, 754, 691 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.55 (d, 2H, aromatic), 7.46 (d, 2H, aromatic), 7.35 (m, 3H, aromatic), 7.18 (d, 2H, aromatic), 2.61 (t, 2H), 1.69-1.55 (m, 2H), 1.40-1.21 (m, 10H), 0.91 (t, 3H); ^{13}C NMR (CDCl$_3$) δ 143.42, 131.52, 131.48, 128.44, 128.28, 128.02, 123.47, 120.32, 89.58, 88.69, 35.91, 31.87, 31.26, 29.45, 29.25, 22.67, 14.11.

Procedures

Polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under dry nitrogen with the use of TaCl$_5$-*n*-Bu$_4$Sn catalyst which is the most powerful in the polymerization of diphenylacetylenes (6). Copolymers were isolated by precipitation into a large amount of methanol, and the copolymer yields were determined by gravimetry. The conversions of comonomers **2a-c** were determined by gas chromatography (GC) using docosane as internal standard, while that of **1** could not be evaluated since its boiling point was too high. A detailed procedure of the polymerization has been described elsewhere (9). Oxidative cyclodehydrogenation and its work-up were performed according to reference (3).

Measurement

The molecular weights of copolymers were evaluated by GPC [eluent, $CHCl_3$; columns, Shodex K-803, K-804, K-805 for low molecular weight polymers, and Shodex K-805, K-806, K-807 for high molecular weight polymers (Showa Denko, Co., Japan)]. IR, UV, and NMR spectra were measured on a Shimadzu FTIR-8100 spectrophotometer, a Jasco V-530 spectrophotometer, a JEOL EX-400 spectrometer, respectively. Thermogravimetric analyses (TGA) were carried out with a Perkin Elmer TGA-7 analyzer (in air, heating rate 10 °C/min).

Results and discussion

Copolymerization of diphenylacetylene having hexaphenylbenzene group

Table 1 summarizes the results of the copolymerization of **1** with diphenylacetylenes **2a-c**. No polymer was obtained in the homopolymerization of **1** by $TaCl_5$-*n*-Bu_4Sn (run 1). This result is attributable to the steric hindrance of **1**. On the other hand, copolymerization of **1** with **2a** proceeded at various feed ratios to give copolymers in relatively good yields. The copolymer obtained in run 3 (**1/2a** in the feed = 25/75) was soluble in $CHCl_3$ and its M_w reached a relatively large value of 31×10^4. A free-standing film could be fabricated by solution casting. On the other hand, when **1** was 20 mol% in the feed, the copolymer was insoluble (run 4), which is compatible with the finding that poly(**2a**) is insoluble in any solvent. Since poly(**2b**) and poly(**2c**) are completely soluble in common organic solvents unlike poly(**2a**), it is expected that the use of **2b** and **2c** as comonomers is effective in enhancing copolymer solubility. When copolymerizations were carried out at a feed ratio of **1/2b**, **2c** = 5/95 (runs 6, 7), copoly(**1/2b**) and copoly(**1/2c**) were obtained in good yields, and were completely soluble in toluene and $CHCl_3$. Their M_w values were as high as ca. 1×10^6 and free-standing films could be

Table 1. Copolymerization of **1** (M_1) with **2a–c** (M_2) by $TaCl_5$–*n*-Bu_4Sn at various feed ratios [a]

run	M_1 in feed	$[M]_{0,total}$	convn. of M_2	polymer [b]		
	mol%	M	%	yield, wt%	$M_n/10^{4}$ [c]	$M_w/10^{4}$ [c]
			Comonomer: **2a**			
1	100	0.050	–	0	–	–
2	50	0.10	79	16	3.6	7.3
3	25	0.10	62	17	19	31
4	20	0.20	71	45	insoluble	
5	0	1.0	100	71	insoluble	
			Comonomer: **2b**			
6 [d]	5	0.20	100	61	20	110
			Comonomer: **2c**			
7 [d]	5	0.20	100	62	20	100

[a] Polymerized in toluene at 80 °C for 24 h; $[TaCl_5]$ = 10 mM, $[n\text{-}Bu_4Sn]$ = 20 mM.

[b] MeOH-insol. product. [c] By GPC. [d] $[TaCl_5]$ = 20 mM, $[n\text{-}Bu_4Sn]$ = 40 mM.
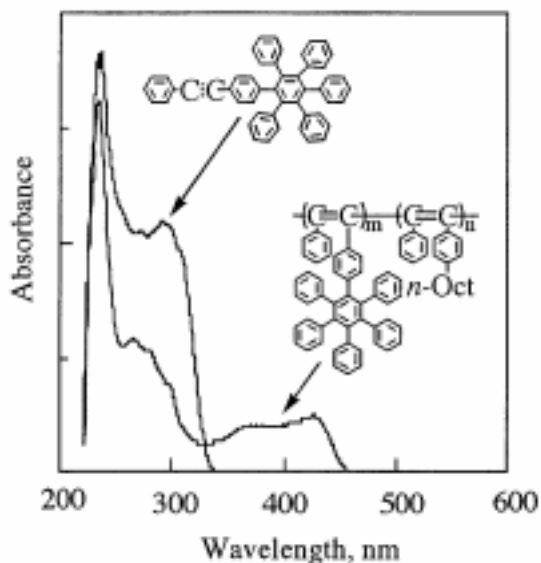
Figure 1. UV-vis spectra of 1 and copoly-(**1/2c**) (in THF).
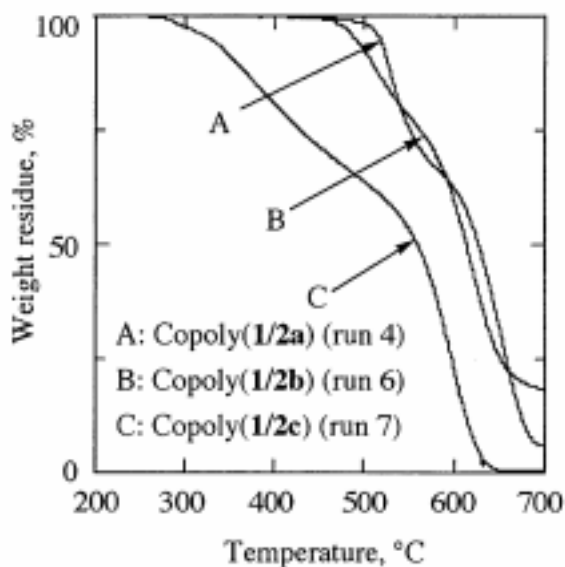
Figure 2. TGA curves of the copoly-(**1/2a–c**) (heating rate 10 °C/min, in air).

fabricated.

Structure and properties of copolymers

In the IR spectrum of the present copolymers, no absorption was observed around 2200 cm^{-1} ($\nu_{C\equiv C}$) which is seen in the monomers. Otherwise, the spectra of the copolymers were close to superpositions of the spectra of **1** and the comonomers. ^{1}H NMR spectra showed only very broad signals due to the high viscosity of copolymer solutions because of their high molecular weight, and no useful information was available.

Figure 1 depicts the UV-vis spectra of **1** and copoly(**1/2c**). Copoly(**1/2c**) has two absorption maxima in the region of 370-450 nm, and the cutoff wavelength is ca. 460 nm. All the copolymers showed similar spectra, and they were basically the same as those of other poly(DPAs) reported before. These spectra correspond to the yellow to orange color of the copolymers.

Thermogravimetric analyses (TGA) of the present copolymers were conducted in air (Figure 2). Copoly(**1/2a**) (run 4) and copoly(**1/2b**) (run 6) were fairly thermally stable, and no weight loss was observed up to ca. 420 °C. On the other hand, copoly(**1/2c**) (run 7) began to lose weight at 260 °C, and hence the *n*-octyl group proves to considerably reduce the thermal stability.

Copoly(**1/2a**) was subjected to the oxidative cyclodehydrogenation reaction under the conditions shown in Scheme 3. The reaction proceeded to give an insoluble dark-brown product. Thus, the solubility and color of the polymer considerably changed with this reaction. Similar changes have been observed with the same reaction of a vinyl copolymer containing hexaphenylbenzene moieties (3a). These features indicate that the cyclodehydrogenation reaction has proceeded with copoly(**1/2a**) as well.

Acknowledgment

References

1. (a) Mukamal H, Harris FW, Stille JK (1967) J Polym Sci Part A-1 5: 2721 (b) Harris FW, Stille JK (1968) Macromolecules 1: 463 (c) Stille JK, Harris FW, Rakuits RO, Mukamal H (1966) J Polym Sci Part B 4: 791
2. (a) Iyer VS, Wehmeier M, Brand JD, Keegstra MA, Müllen K (1997) Angew Chem Int Ed Engl 36: 1604 (b) Müller M, Iyer VS, Kübel C, Enkelmann V, Müllen K (1997) Angew Chem Int Ed Engl 36: 1607 (c) Müller M, Mauermann-Düll H, Wagner M, Enkelmann V, Müllen K (1995) Angew Chem Int Ed Engl 34: 1583
3. (a) Kübel C, Chen S-L, Müllen K (1998) Macromolecules 31: 3014 (b) Wolfe JF, Arnold FE (1981) Macromolecules 14: 909 (c) Wolfe JF, Loo BH, Arnold FE (1981) Macromolecules 14: 915
4. Shirakawa H, Masuda T, Takeda K (1994) The Chemistry of Triple-Bonded Functional Groups In; Patai S, (ed), Wiley, Chichester (supplement C2, Chapter 17)
5. Niki A, Masuda T, Higashimura T (1987) J Polym Sci Part A, Polym Chem 25: 1553
6. (a) Kouzai H, Masuda T, Higashimura T (1994) J Polym Sci Part A, Polym Chem 32: 2523 (b) Tsuchihara K, Masuda T, Higashimura T (1992) Macromolecules 25: 5816
7. (a) Zheng Q, Sun R, Zhang X, Masuda T, Kobayashi T (1997) Jpn J Appl Phys 36: 1675 (b) Tada K, Hidayat R, Hirohata M, Teraguchi M, Masuda T, Yoshino K (1996) Jpn J Appl Phys 35: 1138 (c) Hidayat R, Hirohata M, Tada K, Teraguchi M, Masuda T, Yoshino K (1997) Jpn J Appl Phys 36: 3740
8. (a) Suzuki H, Kondo A, Inoue M, Ogawa T (1984) Synthesis 121 (b) Suzuki H, Kondo A, Ogawa T (1985) Chem Lett 411
9. Ito H, Masuda T, Higashimura T (1996) J Polym Sci Part A, Polym Chem 34: 2925