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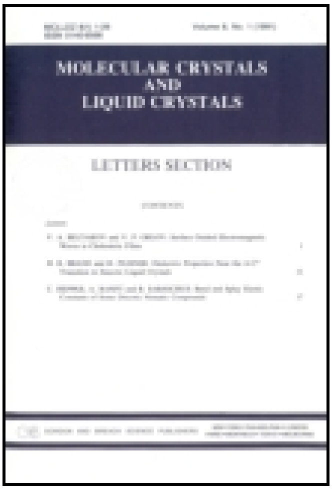

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Study for Soluble and Low-Refractive Index Hyperbranched Polymer Consisting of Fluoroadamantane

Sunnam Kim[a], Kensuke Kuroda[a], Yutaka Kuwahara[a], Tomonari Ogata[b], Yagi Ryohei[a] & Seiji Kurihara[acd]

[a] Department of Applied Chemistry and Biochemistry, Graduate School of Science and Technology, Kumamoto University, Kumamoto, Japan

[b] Innovative Collaboration Organization, Kumamoto University, Kumamoto, Japan

[c] Kumamoto Institute for Photo-Electro Organics (PHOENICS), Higashi-ku, Kumamoto, Japan

[d] JST-CREST, K's Gobancho, Chiyoda-ku, Tokyo, Japan

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Study for Soluble and Low-Refractive Index Hyperbranched Polymer Consisting of Fluoroadamantane

SUNNAM KIM,[1,*] KENSUKE KURODA,[1]
YUTAKA KUWAHARA,[1] TOMONARI OGATA,[2]
YAGI RYOHEI,[1] AND SEIJI KURIHARA[1,3,4,*]

[1]Department of Applied Chemistry and Biochemistry, Graduate School of Science and Technology, Kumamoto University, Kumamoto, Japan
[2]Innovative Collaboration Organization, Kumamoto University, Kumamoto, Japan
[3]Kumamoto Institute for Photo-Electro Organics (PHOENICS), Higashi-ku, Kumamoto, Japan
[4]JST-CREST, K's Gobancho, Chiyoda-ku, Tokyo, Japan

Soluble hyperbranched polymers consisting of numerous functional groups and end groups were prepared by one pot synthesis of divinyl monomers in a large amount of chain transfer agent (CT). The polymerization conditions for control of molecular weight with suppression of a gelation were investigated at various concentrations of reactants and molar ratio of CT to monomer. Hyperbranched polymers consisting of numerous functional groups and end groups were synthesized and molar ratio of end groups Hyperbranched polymers were evaluated by analysis of TOF MS and NMR. Transparent and low refractive index thin film was easily obtained by polymerization of divinyl fluoroadamantane monomers.

Keywords Low refractive index; hyperbranched polymer; fluoroadamantane; telomerization

Introduction

The refractive index, a most fundamental quantity in optics and optoelectronics, determines many figures of merit of optical components. Low refractive index materials have been widely employed as optical waveguides, low-k materials, and anti-reflection coatings [1–4]. Fluorinated polymers such as Teflon (by DuPont Co) and CYTOP (by Asahi glass Co) are well known as low refractive index materials stem mainly from fluorine atom with low refraction. However, common fluoropolymers exhibit limited fabrication and application

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[*] Address correspondence to Sunnam Kim and/or Seiji Kurihara, Department of Applied Chemistry and Biochemistry, Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto, 860-8555, Japan. E-mail: sn-kim@kumamoto-u.ac.jp, kurihara@kumamoto-u.ac.jp

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with poor solubility and poor adhesion / softness based on the thermal and chemical resistance [5].

On the other hand, hyperbranched polymers (HBP) containing numerous functional groups per a unit molecule show intrinsic good solubility and low viscosity of solution with respect to the absence of chain entanglements [12]. Modification of the number and type of functional groups on the HBPs is able to control their solubility, compatibility, reactivity, adhesion to various surfaces, self-assembly, chemical recognition, and electrochemical and luminescence properties, a powerful tool for a wide variety of applications.

As a method of HBP polymerization, radical polymerization of a divinyl monomer under high initiator concentration has been reported [13–14]. It can be carried out by one pot synthesis and it is easy way to obtain soluble HBP. However, much fraction of initiator fragments in HBP is to be unnecessary groups to the functional groups, although it helps to suppression of gelation with controlled molecular weight. In order to enhance functionality of HBP with high contents of functional groups, end groups can be substituted by functional groups. On this point of view, telomerization to control the molecular weight by chain transfer reaction is very useful method to modify end groups of HBP with various structures, because chain transfer agent (telogen) can be quite freely designed to various structures [15–17].

Furthermore, it is considered that a molar volume (the density of polymers) is an important factor determining the refractive index of materials [6–11]. Namely, fluorinated adamantane polymer is expected for a promising low refractive index material as well as excellent transparency, since adamantane consisting of carbon cage molecules as rigid structure has lower packing with many cavities. In this study, we synthesized soluble HBPs having fluorinated adamantane groups and telogen end groups and evaluated the architecture of HBPs concerned with the contents of end groups. In addition, their refractive indices were investigated with various polymerization conditions.

Experimental

Materials

1,3-Adamantanediol diacrylate (AdDA) and perfluoro-1,3-adamantanediol dimethacrylate (F-AdDMA) were supplied from Idemitsu kosan Co. Ltd. All reagents were purchased from general chemical industries.

Polymerization

Monomers of methyl methacrylate(MMA), ethylene dimethacrylate (EGDMA), AdDA or F-AdDMA were respectively polymerized in the present of 2,2′-azodiisobutyronitrile (AIBN) as an initiator and benzyl mercaptan as a chain transfer agent (CT) with various concentration in toluene solvent at 80°C for 5 hours under nitrogen atmosphere. The products were obtained by reprecipitation in large amount of methanol.

Characterization

Molecular structures were determined by ^{1}H-NMR spectroscopy (JEOL JNM-EX400; 400 MHz). An autoflex III, time of flight mass spectrometry with the method of matrix assisted laser desorption/ionization (MALDI TOF-MS; Bruker Daltonics, Bremen, Germany) equipped with smartbeam laser was used for mass analysis. The smart beam laser a special beam shape which is dynamically modulated and can acquire high signal intensity from small amount samples. All spectra in this report were measured in positive reflectron mode. Acceleration and reflectron voltages were 19 and 21 kV, respectively. Instrument control and basic data handling was performed with flexControl and flexAnalysis 3.0 software.

Molecular weight of polymers were measured by gel permeation chromatography (GPC; JASCO RI930, 870UV (254 nm), 880PU, 865CO Shodex DEGAS, KF-804L (polystyrene standard), THF eluent (HPLC grade), 40°C, 1ml/min).

Absorption spectra were recorded on a UV-vis absorption spectroscope (Perkin Elmer Lambda 650). Refractive indices of films on silicon substrate were measured by ellipsometry (Otsuka Electronics FE-5000S).

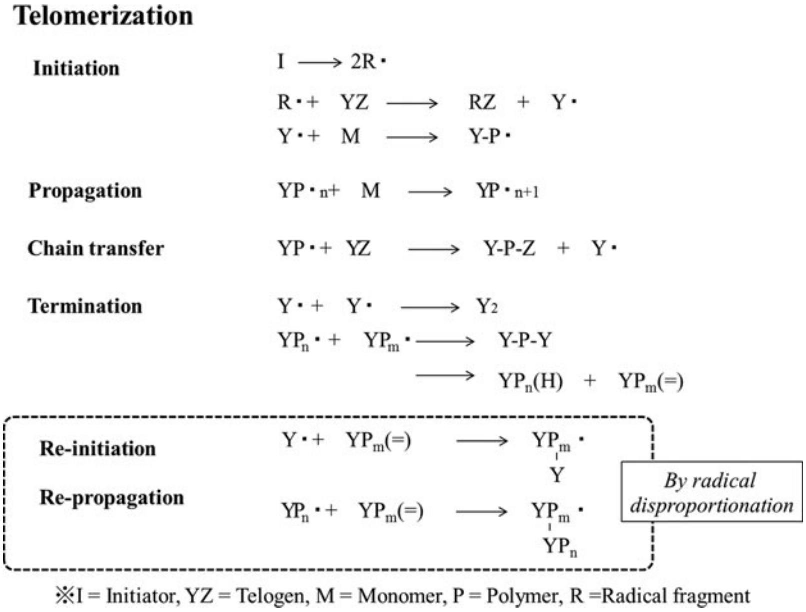
Sample Preparation for MALDI Analysis

The obtained polymer was analyzed using dithranol (from Sigma-Aldrich, Tokyo, Japan) as matrix and sodium trifluoroacetate (NaTFA, from TCI, Tokyo, Japan) was added to assist sample ionization. The obtained polymers and dithranol were respectively dissolved at 10 mg/ml in acetone and sodium trifluoroacetate (NaTFA, from TCI, Tokyo, Japan) was dissolved at 1 mg/ml in acetone. The prepared solutions were mixed by a volume ratio of 1:1:3. The mixture solutions were applied to the stainless steel slide and the solvents were allowed to evaporate off.

Results and Discussion

Telomerization in the Present of a Cross Linker

Telomerization (Scheme 1) is a kind of radical polymerization to control the molecular weight of polymer. For much high concentration of chain transfer agent (CT), termination with radical disproportionation drastically occurs and allows radical re-initiation or

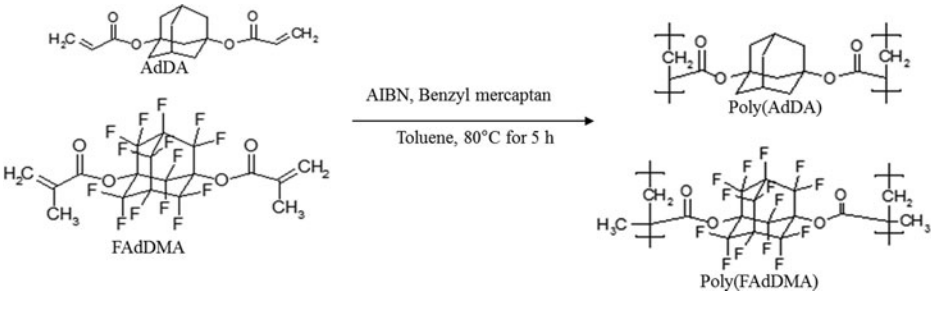


Scheme 1. Telomerization process.

Table 1. Telomerization condition and molecular weight of HBP-MMA. Telomerization of 2 mol/L of MMA was carried out in toluene at 80°C for 5 h with CT

	Molar ratio of							
Entry	MMA	EGDMA	Benzyl mercaptan	AIBN	Mn GPC	Yield (g)	Yield (%)	Appearance
P1	100	1	10	1	1500	2.24	44.8	Soluble polymer
P2	100	1	1	1	7000	3.39	67.8	Soluble polymer
P3	100	1	0	1	32000	4.3	86	gel
P4	100	0	1	1	4400	3.44	68.8	Soluble polymer

re-propagation reaction. Although radical polymerization in the present of a cross linker results in growth to network structure, gelation can be prevented by restriction of molecular weight. In order to obtain highly soluble HBP, herein, we sought the appropriate polymerization conditions. The polymeric properties such as solubility and molecular weight were largely dependent on the concentration of monomer and CT as shown in Table 1. Without CT, gelation was reasonably occurred in the present of cross linker of EGDMA (P3 in Table 1). When benzyl mercaptan was incorporated as a CT and telomerizations of MMA were carried out without cross linker, the molecular weights were well controlled as Mn = 4400, (P4 in Table 1, Mn = the number average molecular weight). In the present of a cross linker with 1% of CT concentration, soluble HBPs in the most of polar solvents were obtained and the solution exhibited low viscosity. The molecular weights were dependent on the concentration of CT (P1 and P2 in Table 1). In conclusion, gelation was suppressed by adding CT and a network structure of HBP having many end groups was obtained.



Scheme 2. Schematic polymerization of poly(AdDA) and poly(FAdDMA).

Dependence of Molecular Weight

For the polymerization of EGDMA as a divinyl monomer, molecular weight and molar ratio of end groups were investigated with various CT concentrations, where concentrations of initiator and cross linker were fixed to 1% of monomer at 1.5 M. When molar ratio of CT to monomer was more than 1.2, soluble polymers were obtained without gelation. Molecular weights and the distributions were measured by GPC and the results are summarized in Table 2. At 1:1.2, broad peak exhibiting Mn = 42000 was observed without low molecular weight peak. Molecular weights were shifted to the lower molecular weight region by increase of CT concentration. When molar ratio of CT to monomer was 1:1.5, obtained HBP showed broad molecular weight distribution. When EGDMA: CT = 1:4, Mn = 1900 with low molecular weight distribution.

Evaluation of Molar Ratio of End Group

As the MALDI trace shows that the individual polymer molecules with the accuracy in mass determination, the principal peaks are separated largely depending on the number of repeated units and end group. So, it is useful method for analysis of polymer structure such as average molecular weight (Mw) and end group composition calculations. To simplify the analysis of polymer structure, EGDMA of cross linker was used as divinyl monomer. Mw of polymer consisting of n number of EGDMA and m number of telogen and x number of H as end groups can be calculated as: $198\ n + 123\ m + x$. If the polymer was ionized with Na+, their mass shall be given by $198\ n + 123\ m + x + 23$. From the detected molecular weight (m/z) composition ratio of EGDMA monomer to benzyl group as fragment of CT end group was estimated. The composition ratios of monomer unit group to end group was in the range between 5:5 and 7:7 as summarized in Table 3. Thus the sizes of HBP units were expected and most of polymers consist of 50% of CT fragment as end groups.

Architecture of polymers was also determined by ^{1}H-NMR as shown in Figure 1, as benzene group of fragment of CT is distinguished with methylene group of monomer. By the analysis of ^{1}H-NMR profiles, the composition ratio of end group to monomer unit was almost 1:1 and end group contents to monomer unit tended to increase with increase of CT concentration as shown in Table 4. It agreed well with the result of TOF MS analysis.

Low Refractive Index HBP Film

For a low refractive index material, HBPs consisting of fluorinated adamantane cage, poly(AdDA) and poly(F-AdDMA) with Mw 2000, were prepared by polymerization of divinyl adamantane monomers as similar condition mentioned above and results were descried in Table 5. By spin coating method, the transparent and thin films were easily prepared and their transmittances were almost 100% in the visible light range as shown in Figure 2. Refractive indices of poly(AdDA) and poly(F-AdDMA) films were respectively determined as 1.56 and 1.41. For the refractive index of poly(F-AdDMA) film (1.41), it was lower than those of general polymers such as PMMA (1.5) and PS (1.58). In the future study to obtain much lower refractive index HBP film, we are considering the introduction of CT consisting of fluorinated group.

Table 2. Polymerization condition of EGDMA with various concentration of benzyl mercaptan in toluene at 80°C for 5 h and the results

Entry	Molar ratio (EGDMA/Benzyl mercaptan/AIBN)	Infeed into 10 ml toluene			Appearance of obtained product	Yield (%)	Mn	Mw	Mw/Mn
		EGDMA (g)	Benzyl mercaptan (g)	AIBN (g)			determined by GPC		
HBP1	(1/1/0.01)	3	1.88	0.0248	Gel	89	—		
HBP2	(1/1.1/0.01)	3	2.07	0.0248	Gel	82.3	—		
HBP3	(1/1.2/0.01)	3	2.26	0.0248	Soluble polymer	49.3	42000	90000	2.14
HBP4	(1/1.5/0.01)	3	2.82	0.0248	Soluble polymer	77.3	5000	20000	4
HBP5	(1/2/0.01)	3	3.76	0.0248	Soluble polymer	32.3	2700	4600	1.7
HBP6	(1/4/0.01)	3	7.52	0.0248	Soluble polymer	20	1900	2300	1.2

Table 3. Structural analysis with the ratio of EGDMA/Benzyl mercaptan group for PEGDMA from the results of TOF-MS

Polymer	m/z	1505	1629	1753	1827	1951	2076	2149	2275
	Composition ratio of Methylene : Benzyl	5:04	5:05	5:06	6:05	6:06	6:07	7:06	7:07
HBP3 (1:1.2)	m/z peak intensity	+++	+++++	++	+++++	+++++	++	+++++	++++
HBP4 (1:1.5)		+++	+++++	+++	++++	++++	++	+++	+++
HBP5 (1:2)		+++	+++++	++++	++++	+++++	+++	++++	++++
HBP6 (1:4)		+	++++	+++++	++	+++++	++++	++	++++

*Signal intensity : +++++ > ++++ > +++ > ++ > +

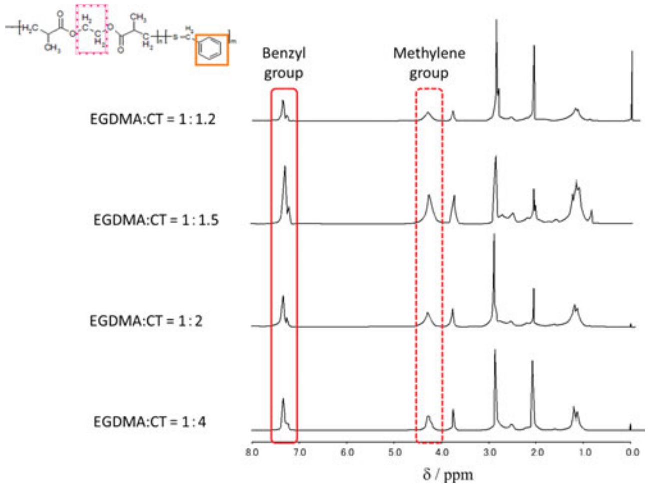


Figure 1. Molecular structures and ^{1}H-NMR spectra of HBPs when EGDMA: CT = 1:1.2, 1:1.5, 1:2, 1.4.

Table 4. Composition ratio of end group to EGDMA unit, estimated by ^{1}H-NMR

Polymers	Composition ratio of end group to EGDMA unit
HBP3 (1:1.2)	0.82
HBP4 (1:1.5)	0.83
HBP5 (1:2)	0.91
HBP6 (1:4)	1.1

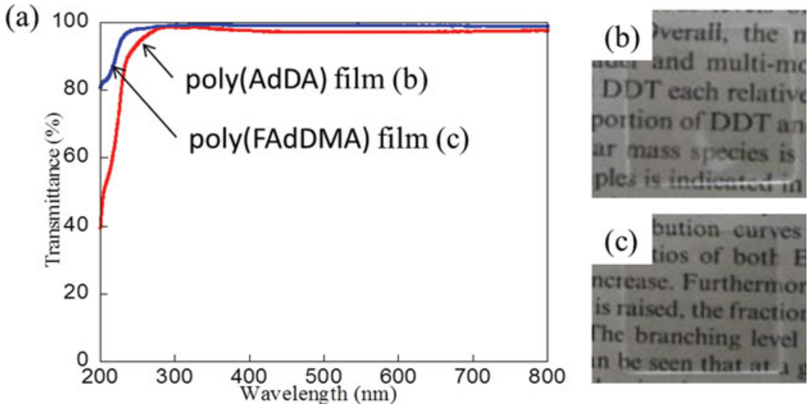


Figure 2. (a) Transmission spectra and the pictures of (b) poly(AdDA) and (c) poly(FAdDMA) films on glass substrate.

Table 5. Polymerization condition of AdDA and F-AdDMA

Polymers	Molar ratio (monomer/Benzyl mercaptan/AIBN)	Infeed (solvent: Toluene 5 ml)			Yield (%)	Mn⋇	Mw/Mn
		Monomer (g)	Benzyl mercaptan (g)	AIBN (g)			
A1	(1/0.8/0.01)	AdDA 0.5	0.18	0.005	38	2700	2.89
A2	(1/1.0/0.01)	AdDA 0.5	0.22	0.005	32	2100	1.97
A3	(1/1.5/0.01)	AdDA 0.5	0.34	0.005	26	1900	1.53
A4	(1/1.0/0.01)	F-AdDMA 0.5	0.11	0.005	10	2200	4.12

⋇determined by GPC.

Conclusion

Polymerizations of EGDMA were carried out with various molar ratio of benzyl mercaptan as telogen to monomer unit. Highly soluble hyperbranched polymers were obtained and contained about 50% of telogen end groups. For HBP consisting of fluorinated adamantane cage, transparent thin film was obtained and the refractive index was 1.41. With CT containing fluorinated group, lower refractive index HBP film is promisingly expected.

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