Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 05 Dec 2006.

To cite this article: Michiya Ota , Masaharu Fujii , Tetsuya Horiguchi , Sugio Otani , Akira Kojima & Yutaka Takahashi (1995): Preparation and Characterization of Polyfluoro-Triarylmethane Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 272:1, 167-174

To link to this article: http://dx.doi.org/10.1080/10587259508055285

Mol. Cryst. Liq. Cryst., 1995, Vol. 272, pp. 167–174
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Preparation and Characterization of Polyfluoro-Triarylmethane Polymers

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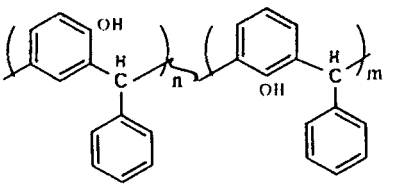
Abstract A polyfluorotriarylmethane polymer was prepared by the reaction of 3,5-difluorophenol (3,5-DFPh) with pentafluorobenzaldehyde (PFBA).The polymer obtained was characterized by NMR, FT-IR, UV-Vis, MS and Gel Permeation Chromatography (GPC). It was found that phenolic ring in the polymer was connected at meta-position by methine carbon, and that molecular weight distribution of the polymer consists of mainly four components ranging from 6,000 to ca. 1,000,000. Further oxidation of this polymer generates the radicals which are stable in air for at least 3 months.

INTRODUCTION

Meta-connected triarylmethane polymers[1] are known as precursors of potential ferromagnets[2]. Magnetically interesting behavior has been previously observed for the poly-radicals resulting from dehydrogenation of triaryl-methane polymers I and II[1,3].



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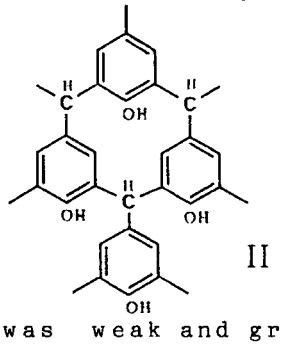


II

However, the magnetic property was weak and gradually disappeared within several months. The structures of these amorphous polymers were so intricate that the origin of

the magnetic properties could not be clearly analyzed.

Because of the thermal stability of fluorinated polymers, polyfluorotriarylmethane polymers **III**, **IV**, **V**, and **VI** depicted in Figure 1 are anticipated to generate thermally and chemically stable polyradicals[4]. The preparation and characterization of polyfluorotriarylmethane polymer **III** are described in this report, because this polymer can be synthesized more easily than others.

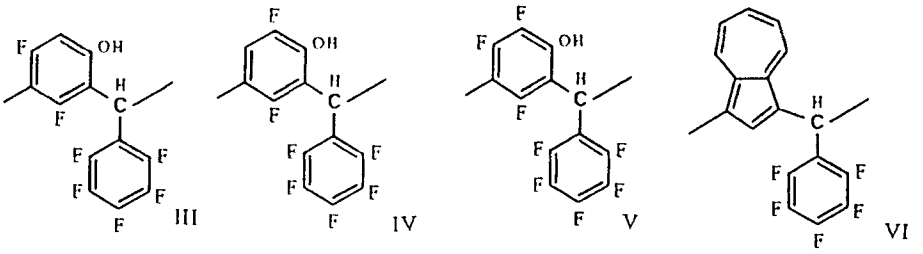


Fig.1 Typical unit structures of polyfluorotriarylmethane polymers[5].

The present paper describes polyradical formation from the polyfluorotriarylmethane polymers as a synthetic approach to organic ferromagnet based on Itoh and Mataga model[2].

EXPERIMENTAL

1.Preparation

The handling of the materials used during this study was performed most carefully to be free from contamination by inorganic ferromagnetic species.

Pentafluorobenzaldehyde (PFBA) was purified by vacuum distillation and 3,5-difluorophenol (3,5-DFPh) was distilled under atmospheric pressure. The polymer was prepared from 3,5-DFPh and PFBA under the conditions shown in Table 1. Phenol/ benzaldehyde polymer was also prepared in order to compare with 3,5-DFPh/PFBA polymer.

The mixture of 3,5-DFPh, PFBA and acid catalyst was heated at 130 ^{o}C with stirring under argon atmosphere. The resulting polymer was stirred in 20 ml of tetrahydrofurane (THF) and then the residue insoluble in THF was

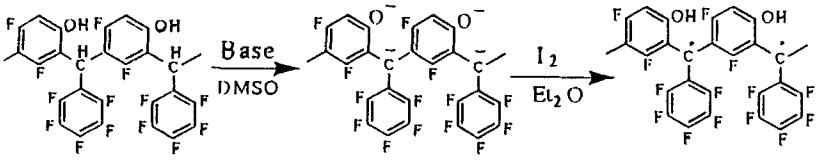
Table 1 Composition and condition of polyfluorotriarylmethanepolymers.

Monomers	Monomer/PFBA (molar ratio)	Acid*1 (wt%)	Reaction Temp.(°C)	Reaction Time(min)	Yield*2 (%)
3,5-DFPh	1/2	2	130	120	40
Ph	1/1.25*3	1	130	120	70

*1 PTS : p-Toluenesulfonic acid.
*2 Yield : purified polymer/(Monomer+PFBA) x100(%).
*3 Molar ratio of Monomer/benzaldehyde.

removed by filtration. Reddish precipitate was taken out by pouring the filtrate into cyclohexane. The light-yellowish powder was obtained, followed by reprecipitating with distilled water from ethanol solution of the reddish precipitation.

We expect that the polymer polyradicals can be obtained by oxidizing with iodine after the treatment with NaH in 15% dimethylsulfoxide/diethylether solution (Scheme 1).



(1)

2. Characterization

Monomers and polymers were detected by FT-IR (Perkin Elmer, Paragon 1000), ^{1}H-NMR (Varian, Gemini 200), and Field Desorption (FD) and Laser Desorption-Time of Flight (LD-TOF) Mass(JEOL, JMS-LD 1700) spectra. Molecular weight distribution of the polymers in THF solution was determined by gel permeation chromatography (GPC, polystyrene standard, Shimadzu, LC 6AD GPC system). UV-Visible spectra were also recorded on a JASCO Ubest-50 spectrometer. Electron spin resonance (ESR) of the polyradical powders was measured with a JEOL RE2X at room temperature.

RESULT AND DISCUSSION

1. Reaction and structure of polyfluorotriarylmethane polymers

Table 1 shows that fluorine-containing phenol, DFPh is less reactive than phenol and that the yield of the resulting polymer is lower than that of Ph/BA polymer. These polymers were soluble into organic polar solvents such as THF, methanol, ethanol, and DMSO.

Polymers insoluble into the above polar solvents were obtained by heating for longer period, at higher temperatures, or in the presence of excess acid catalyst than those in Table 1. Such polymers seem to consist of rigid, three dimensional network structure which has been observed for phenol/formaldehyde resin. It is, consequently, expected that the polymers soluble in polar solvents prepared under the conditions of Table 1 consist of linear chain structure without crosslinking.

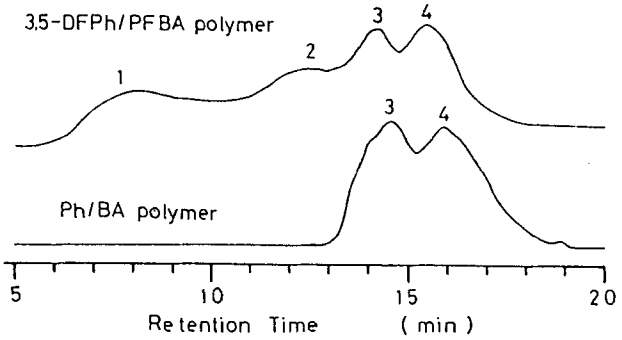


Figure 2 Molecular weight distribution of 3,5-DFPh/PFBA and Ph/BA polymers. (Mobile phase: THF)

Figure 2 shows the molecular weight distribution of the 3,5-DFPh/PFBA and Ph/BA polymers. The molecular weight distribution of 3,5-DFPh/PFBA polymer was consisted of four eluted peaks and the first elution (peak 1) was detected over the retention time from 6 to 8 min. The retention time of two peaks, 3 and 4, was similar to that of Ph/BA. Table 2 shows the molecular weight of these polymers calculated from the retention time of peak maximum using calibration curve with polystylene. It is, therefore, concluded that the 3,5-DFPh/PFBA polymer also contains larger molecular weight component, compared with that of Ph/BA.

Although the amorphous structure of these polymers is essentially complicated by the entanglement between long molecular chains, the chemical structures closely

Table 2 The molecular weight of the polymers converted from calibration curve with polystylene.

Polymer	Molecular Weight			
	Peak 1	Peak2	Peak3	Peak4
3,5-DFPh/PFBA	1,680,000*1	102,400	25,000	6,250
Ph/BA*2	-	-	12,000	3,390

*1 It was determined with dimethylformamide including 10 mmol/l of LiCl as mobile phase.

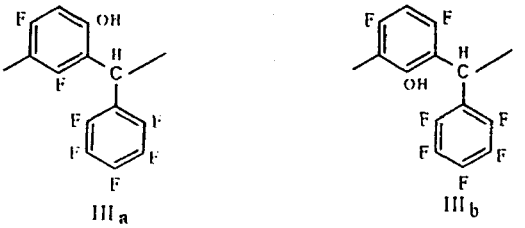
*2 No peaks corresponding to the peaks 1 and 2 of the 3,5-DFPh/PFBA polymer were detected in the Ph/BA polymer.

related to the electrophilic reaction of carbocation produced by aldehyde group in PFBA with phenolic rings.

The reaction mechanism of 3,5-DFPh with PFBA was investigated by the calculation of a charge and an electron density of each atom in DFPh with MNDO/PM3 method. Table 3 shows that charges of aromatic carbon in 3,5-DFPh are small at C2, C4, and C6, and hence it can be presumed that these carbons are subjected to attack of electrophiles. In this reaction, the carbocation resulting from PFBA in the presence of acid catalyst behaves as an electrophile and will attack electrophilically C2 since the charge of C2 is lowest among C2, C4, and C6. Furthermore, a small difference of the atomic charge in mono-substituted phenolic ring between -0.2207 of C4 and -0.2085 of C6 was anticipated by the MNDO/PM3 calculation[7]. The polymerization proceeds by the second electrophilic substitution to the mono-substituted phenolic ring. It is difficult to specify the position of C4 or C6 in phenolic ring at which the substitution takes place. Therefore, the polymer may contain structural isomers such as IIIa and IIIb shown in Figure 3, which are essentially connected at meta-positions in the aromatic ring.

According to the assignments of FT-IR spectra to the polymers in Table 4, the absorption of CH deformation vibration of out-of-plane represents the characteristic of meta-connected triarylmethyl structure predicted from the calculated data with MNDO/PM3 in Table 3.

The isomers IIIa and IIIb in Figure 3 can not be distinguished by FT-IR spectra, nor by ^{1}H-NMR spectra. CH



IIIa IIIb

Figure 3 Structural isomers of meta-substituted polymer.

Table 3 Calculated electron density and charge of 3,5-DFPh (MNDO/PM3).

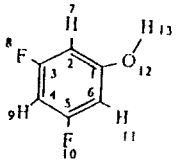
Structure	Atom	Charge	Electron Density
	C1	0.1538	3.8462
	C2	-0.2490	4.2490
	C3	0.1366	3.8634
	C4	-0.2116	4.2116
	C5	0.1316	3.8684
	C6	-0.1939	4.1939

Table 4 FT-IR spectra of 3,5-DFPh/PFBA and Ph/BA.

Assignment (cm^{-1})	Polymer	
	3,5-DFPh/PFBA	Ph/BA
1.OH stretching	splitted	splitted
	3430*1 (broad)	3365(shoulder peak)*3
	3600*2 (sharp)	3500(sharp)*4
2.Out-of-plane	850*5	920, 829*6
(CH deformation)		805, 683*7
3.C=O stretching	disappeared	disappeared

*1: interhydrogen bond, *2: intrahydrogen bond, *3: interhydrogen bond (polymeric association), *4: interhydrogen bond (sharp, dimeric association) *5: one isolated ring (substituted at 1,3,4,5,6 positions), *6: one isolated ring (920 cm^{-1}) and two adjacent ring (829 cm^{-1}) (substituted at 1,2,4 positions), *7: three adjacent ring (substituted at 1,2,6 positions)

Deformation vibration of out-of-plane of the Ph/BA polymer, on the contrary, suggests the occurrence of two types of isomeric connection analogous to IIIa and IIIb.

^{1}H-NMR spectrum of 3,5-DFPh/PFBA polymer shows the low field shift of hydroxy proton by intramolecular hydrogen bond formation from 5.4 ppm of monomer to ca. 11 ppm of the polymer. Methine proton interposed between 3,5-DFPhs was observed at around 6 ppm with aromatic proton around 6.5 - 7 ppm. The intramolecular hydrogen bond of

the Ph/BA polymer was not suggested by ^{1}H-NMR spectrum.

LD-TOF mass spectrum less than m/z = 9,000 of the 3,5-DFPh/PFBA polymer under a negative ions detection mode was obtained at intervals of m/z = ca. 300 (formula weight of the repeating unit is 308) from ca. 15,00 to ca.9,000.

No peaks were detected with FD and FAB mass spectrometry.

These results are suggestive of the mixed structure of **IIIa** and **IIIb** in Figure 3. for the 3,5-DFPh/PFBA polymer.

2.Polyradicals from polyfluorotriarylmethane polymer

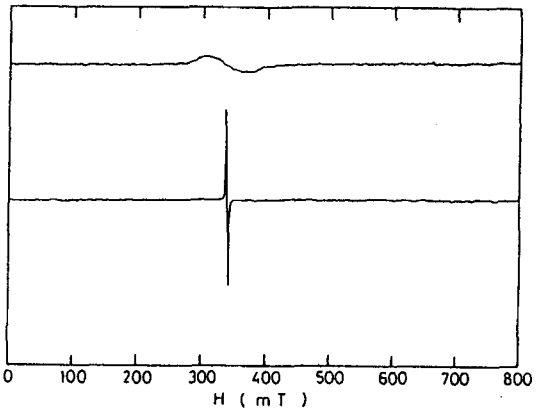


Figure 4 ESR spectra of the radicals from 3,5-DFPh/PFBA polymer.

Figure 4 shows ESR spectra of the polyradicals from 3,5-DFPh/PFBA polymer prepared according to the scheme 1.

The sharp signal of polyradicals with 4 mT of peak-to-peak linewidth, ΔH_{pp} was observed at 338 mT, which is different from the very weak and broad signal of the unoxidized polymer.

The polyradicals are stable more than three months in air. A UV-Visible spectrum showed the absorption at around 500 nm. This is similar to that of perchlorinated triphenylmethyl radical reported by Ballester et al.[6]. According to the UV-Visible spectrum, radical concentration seemed not to be large. Careful examination of FT-IR spectra pointed out that the low radical concentration was caused by the production of quinoid structure (1740 cm^{-1}).

Consequently, the present result on preparation of polyradicals suggests that phenolic OH bring the

satisfactory effect on meta-connection of aromatic ring but at the same time decrease the radical concentration by the formation of quinoid structure.

Also, the stability of radical increased by poly-fluoro-groups.

ACKNOWLEDGMENTS

The authors are deeply indebted to Dr. S.Hashimoto and Dr. R.Akaba (Gunma college of Technology) for valuable discussion, to Prof. T.Takui, Dr. Y.Teki, Dr. D. Shiomi, and Prof. K. Itoh (Osaka City Univ.) for helpful discussion, to Prof. H.Nishide and Dr. T.Kaneko (Waseda Univ.) for the measurement of NMR spectra, to Prof. M.Kinoshita (Tokyo Univ.) for valuable discussion, to Prof. T.Sugawara, Dr. A.Izuoka (Tokyo Univ.) for the valuable discussion, to Mr. Y.Fukai (Fluorine Lab. of Kanto Denka Kogyo Co.,LTD) for helpful discussion about fluorine chemistry, and to Prof. J.S.Miller for useful suggestion. This work was supported by the Grant-in-Aid for Scientific Research on Priority Area "Molecular Magnetism"(Area No.228/04 242 104) from the Ministry of Education, Science and Culture, Japan.

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