Preparation and Characterization of Photosensitive Hyperbranched Aliphatic Polyester

Fei Cao
College of Material Science and Engineering
Hebei University of Science and Technology
Shijiazhuang China
caofei777@aliyun.com

Ling Ling MA
College of Material Science and Engineering
Hebei University of Science and Technology
Shijiazhuang China
malinglinghbkj@163.com

Meng Meng Zhou
College of Material Science and Engineering
Hebei University of Science and Technology
Shijiazhuang China
applezhoumeng@aliyun.com

Jing Du
College of Material Science and Engineering
Hebei University of Science and Technology
Shijiazhuang China
dujinghbkjdx@163.com

Ji Jun Xiao
College of Material Science and Engineering
Hebei University of Science and Technology
Shijiazhuang China
jijunxiao@aliyun.com

Abstract—A novel solvent-free photosensitive polyester based on the hyperbranched aliphatic polyesters has been studied. The hyperbranched aliphatic polyesters (Polymer A), which was prepared from 2,2-dihydroxymethyl butyric acid(DMBA) containing one carboxylic group and two hydroxylic groups, Trimethylolpropane(TMP) and p-toluence sulfonic acid(p-TSA) as a catalyst, of which the degrees of branching (DB) was 0.53 according to definitions by Fréchet. Followed by end-modified with maleic anhydride(MA), end-modified hyperbranched aliphatic polyesters (polymer B) with unsaturated end groups was successfully synthesized. The properties of products were characterized by FI-IR, ^{13}C NMR, GPC, TGA，respectively. The UV-cured Polymer B based on polymer B, 4 wt% 1173 as photoinitiator, and Laromer R TPGDA(6:1) as reactive diluent was obtained, and was exposed for about 1s (2.2KW UV exposure apparatus). Therefore, the UV-cured Polymer B was obtained and regarded as a promising photosensitive material.

Keywords-Hyperbranched aliphatic polyester; solvent-free; 2,2-dihydroxymethyl butyric acid; Photosensitive polyester; Degree of branching

I. INTRODUCTION

One of the exciting and promising developments in material science today is the design and synthesis of hyperbranched polymer materials which are found to have potential applications in the field of functional materials[1-3], such as films[4-5], coatings[6], adesive agents[7], modifiers and so on [8].The candidate materials include polyurethane acrylateand hyperbranched polyester polyamide etc[9]. It is well known that hyperbranched polyester possesses a variety of unique proprieties such as good solubility, low viscosity, multivalence, and encapsulation effects, which mainly are caused by the branching and spherical architecture. In addition, it's well known that hyperbranched aliphatic polyester which mainly synthesis based on 2,2-dimethylol propionic acid (DMPA) as an AB_2 monomer and trimethylolpropane (TMP) as a core moiety. Similarly, 2,2-dihydroxymethyl butyric acid (DMBA) is also a tri-functional compound containing a carboxylic group and two reactive primary hydroxyls, which is also regarded as a ideal model compounds to be used to form new polymer. Whereas, few papers can be found related to DMBA as AB_2 monomer to prepare hyperbranched polymers.

In this paper, a novel hyperbranched polymer was prepared by the DMBA and TMP. The synthesis and characterization of these hyperbrabched polyester and end-modified polyester with carboxyl group and unsaturated C=C double bonds were investigatied, and its application for a photosensitivity polyester, which consists of these polyester and Darocur 1173 as photoinitiator, and TPGDA as reactive diluent, respectively.

II. EXPERIMENT

A. Materials

2,2-dihydroxymethyl butyric acid (DMBA, more than 99.0% purity) was obtained from Jiangxi Nancheng Hongdu Chemical Technology Development Co.,

Ltd.(Nancheng county, Jiangxi Province, China). Trimethylolpropane (TMP) was supplied by Wuhan Youji Industries Co., Ltd (Hubei Province, China). 2-Hydroxy-2-methyl-1-phenyl-1-prop-anone (Darocur 1173) was supplied by Ciba-Geigy, Switzerland. 2-Propenoic acid,1,1'-[(1-methyl-1,2-ethanediyl)bis[oxy(methyl-2,1-ethanediyl)]] ester (TPGDA) was provided by Tianjin Tianjiao Co., Ltd. (Tianjin City, China). p-Toluenesulfonic acid (p-TSA, more than 99.0% purity) was purchased from Lianyungang Ningkang Chemical Co.,Ltd. (Jiangsu Province, China).

B. *Synthesis of Hyperbranched Aliphatic Polyester*

Synthesis of Polymer A: Into a flask equipped with an nitrogen inlet, a thermometer and a reflux condenser, DMBA (13.3 g, 0.09 mol), TMP(1.34g, 0.01mol) and p-TSA (1 wt %) as a catalyst were added. The mixture was heated to 105°Cand stirred at this temperature for 2 h under a stream of nitrogen. Then the nitrogen stream was turned off and the flask sealed and connected to a vacuum line for 2 h, removing the water formed during the reaction. FTIR (KBr, cm-1): 172=O of ester). ^{1}H NMR (500 MHz, Acetone, δ): 0.86 (s, -CH3), 1.66 (s, -CH2-CH3), 3.74,3.79 (s, –CH2-OH), 4.12,4.34 (s, –CH2–O-). ^{13}C NMR (500 MHz, CDCl3, δ): 175.4 (C=O).

Synthesis of Polymer B: In the second step, adequate MA, and hydroquinone (0.007g) as inhibitor were added into the flask to react under a stream of nitrogen at 90°C for about 4h. Then acid value titration was used to pursue the reaction progress of polymer A and MA. Investigations on the acid value titration did not change any longer, which mean that anhydride groups had changed into carboxyl groups completely. At the desired acid value, the polymer B was synthesized. FTIR (KBr, cm-1): 1640 (C=C of polymer B). ^{1}H NMR (500 MHz, Acetone, δ): 6.38(s, -CH=CH-), 13C NMR (500 MHz, CDCl3, δ): 130 (C=C).

C. *Photosensitivity*

Preparation Of UV-cured Polymer B : The Polymer C based on Polymer B, 4 wt% 1173 as photoinitiator, and Laromer R TPGDA(6:1) as reactive diluent was obtained, and was exposed for about 1s (2.2KW UV exposure apparatus).

D. *Characterization*

^{13}C NMR spectra of the synthesized hyperbranched polyesters was recorded on a Bruker Avance-500 MHz spectrometer (Bruker BioSpin, Switzerland). FT-IR spectra were obtained with Nicolet6700/FT-Raman modules, American. Differential scanning calorimetry (DSC) was performed with a Seiko DSC 6200 instrument at a heating rate of 10°C/min-1, in nitrogen. Thermal stability, as measured by 5% weight loss of the polymer samples, was determinded on a Seiko TG/DTA 6200 analyzer at a heating rate of 10°C/min-1, in nitrogen. The molecular weights of the polymers were determined by gel permeation chromatograghy (GPC) relative to polystyrene standards, using tetrahydrofuran (THF) as an eluent.

III. RESULTS AND DISCUSSION

A. *IR analysis*

Figure 1 illustrates the FTIR spectra of polymer A. A new carbonyl absorption corresponding to an ester was observed at 1730 cm-1 while an absorption corresponding to a carbonyl absorption at 1686 cm-1 observed in the monomer disappeared. Thus the present FTIR data support the formation polymer A.

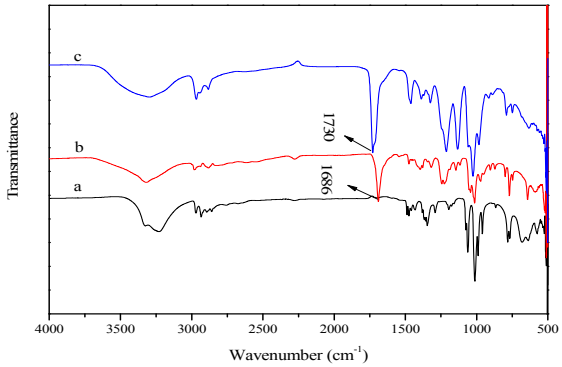

Figure 1. FTIR spectra of TMP(a), DMBA (b) and polymer A(c)

Figure 2 shows the FTIR spectra of polymer B. A broader and considerably stronger absorption band at 1604 cm-1 for Polymer B is attributable to the C=C of MA. hydroxyl (-OH) absorption band became weaker. Anhydride absorption band almost disappears. So the present FTIR data support the formation polymer B.

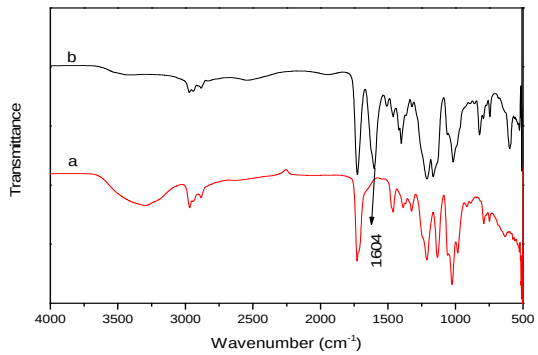

Figure 2. FTIR spectra of polymer A(a) and polymer B(b)

B. *NMR analysis*

The 13C-NMR spectrum of the polymer A is shown in Fig.6. The signals of polymer A should be attributed to the quaternary carbon signals fractions of terminal (T; T=54.058ppm), linear (L; L = 52.456 ppm), and dendritic (D; D =51.631-51.672 ppm, FD =50.497 ppm) fraction, respectively.

The hyperbranched structure is characterized by the average degree of branching (DB) and is one of the most important parameters of hyperbranched polymers, since it is correlated with the density of the hyperbranched structure and the location of the functional groups. The DB of hyperbranched polymers was given by Fréchet [10].

$$DB_{Fréchet} = \frac{D+T}{D+T+L}$$

By integrated intensity of the peaks, So the estimated DB of polymer A from the integration ratio of T, L, D in ^{13}C-NMR spectra can be calculated as 0.53 according to definitions by equation (1).

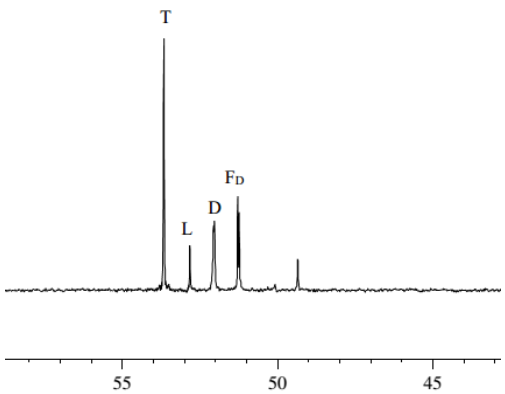

Figure 3. ^{13}C NMR spectrum of the polymer A

The GPC of Polymer A and Polymer B are listed in Table 1. It is clear from Table 1 that the molecular weight of polymer samples generally increased with the addition of MA.

TABLE 1. Molecular Weight of Polymer A and Polymer B

Polymer	M_n	M_w	M_w/M_n
A	1007[a]	1236[a]	1.227
B	1337[b]	1647[b]	1.231

[a] and [b] Determined by GPC in DMF and THE, respectively; polystyrene was used as the standard.

C. Thermal properties

The thermal properties of polymer samples are listed in Table 2 .

TABLE 2. Thermal properties of polymer samples

Polymer	T_g[a](°C)	T_5[b](°C)	T_{10}[b](°C)
A	98.7	209	277
B	-1.3	160	203
UV-cured Polymer B	43.80	209	310

a Determined by DSC.

b the temperature at which 5wt% (T5) and 10wt% of weight loss (T10) were determined by TGA in nitrogen at a heating rate of 10°C/min-1.

From Table 2, It can be seen that the T_g of polymer A was greater than approximately 100°C in comparison to that of the polymer B. The reason is caused by hydrogen bonds. In addition, it is clear that the T_g of UV-cured Polymer B was much higher than that of polymer B. This attributed to the fact that crosslinking of the double bond under the UV irradiation. Similarly, it is clear that the thermal decomposition temperature of UV-cured Polymer B was higher than that of polymer B. It means that the thermal stability of UV-cured Polymer B could be enhanced considerably by crosslinking of the double bond.

D. Photosensitivity of Polymer

After a series of optimization studies, a photosensitive polymer system consisting of polymer B, 1173 (4 wt% of polymer B) and TPGDA(15wt% relative to polymer B) was investigated by a UV exposure apparatus.

Hyperbranched polymer has more double bonds than traditional polymer, so that it can be rapidly crosslinked by exposing under UV light, indicating that the modified UV-curable hyperbranched polyester is a potential material for the application in the photosensitivity materials. The FTIR spectra of polymer B (a), and polymer B (b) with 1173 and TPGDA and UV-cured Polymer B (c) are shown in Fig.4. Clearly, the absorption band at 1604 cm^{-1} represents the C=C double band stretching vibration, and the absorption band gradually weakened, which indicated that extensively C=C double bonds were disappeared.

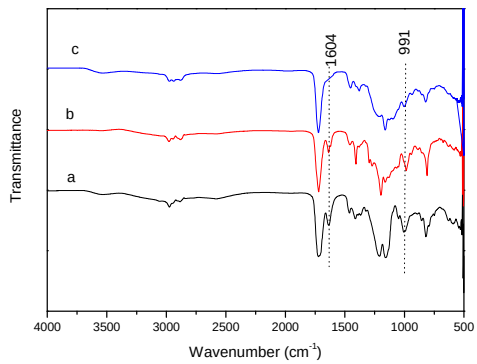

Figure 4. FTIR spectra of Polymer B(a), Polymer C based on polymer B, Darocur 1173 and TPGDA(b) , UV-cured Polymer B (c)

IV. Conclusions

Hyperbranched aliphatic polyester (polymer A) was prepared by polycondensation from symmetric AB_2 monomer, 2,2-dihydroxymethyl butyric acid and trimethylolpropane. Polymer B was achieved by end-capping reaction of polymer A with MA to introduce the C=C double bond at the termini. In addition, the DB of polymer A was calculated from ^{13}C NMR measurement were 0.53. Photosensitive Polymer C based on polymer B, Darocur 1173 (4 wt% of polymer B) and TPGDA (15wt% relative to polymer B) was exposed for about 1 s under a 2.2 KW of full-length UV apparatus, and formed UV-cured polymer film and regarded as a promising photosensitive material.

Acknowledgment

Thanks are due to professors Xiao JiJun for suggestions and for providing the research samples, and to professors Geng YaoZong for their assistance with practical measurements.

References

[1] Y.H. Kim, W.O. Webster, Macromolecules, 25 (1992) 5561-5572.

[2] C.J. Hawker, F Chu, Macromolecules, 29(1996) 4370-4380

[3] V.J. Brigitte, Polym Sci, Part A 38(2000) 2505-2525.

[4] Y. Luo, W. Xin, G. Li, Y. Yang, J. Liu, Y. Lv, Y.J. Jiu, Memb. Sci. 30(2007) 183-193.

[5] Dana M, Dimitrios F, J. Memb. Sci 2008; 310: 512-521.

[6] A.T.M. Rolf, V. Benthem, Prog. Org. Coat. 40 (2000) 203–214.

[7] H. Liu, C.E. Wilen, M. Skrifvars, Reaction of epoxy resin and hyperbranched polyacids, J. Polym. Sci. 38 (2000) 57–65.

[8] D. Schmaljohann, P. Po1tschke, R. Ha1ssler, Blends of Amphiphili -c Hyperbranched Polyesters and Different Polyolefins, Macromolecules . 32 (1999) 6333-6339.

[9] L.J. Hobson, A.M. Kenwright, W.J. Feast, Chem. Commun. (1997) 1877.

[10] C.J. Hawker, R. Lee, J.M. Fréchet, J. Am. Chem. Soc. 131(1991) 4583-4588.