This article was downloaded by:
On: *24 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Preparation and Properties of Aliphatic Polybenzoxazoles from 4,4'-Diamino-3,3'-Dihydroxybiphenyl and Aliphatic Dicarboxylic Acid Chlorides by the Silylation Method

Kazuo Itoya[a]; Michitoshi Arata[a]; Masa-Aki Kakimoto[a]; Yoshio Imai[a]; Jouji Maeda[b]; Toshikazu Kurosaki[b]
[a] Department of Organic and Polymeric, Materials Tokyo Institute of Technology, Meguro-ku, Tokyo, Japan [b] Department of Industrial Chemistry, Tokyo Institute of Polytechnics Iiyama, Atsugi-shi, Kanagawa, Japan

To cite this Article Itoya, Kazuo , Arata, Michitoshi , Kakimoto, Masa-Aki , Imai, Yoshio , Maeda, Jouji and Kurosaki, Toshikazu(1994) 'Preparation and Properties of Aliphatic Polybenzoxazoles from 4,4'-Diamino-3,3'-Dihydroxybiphenyl and Aliphatic Dicarboxylic Acid Chlorides by the Silylation Method', Journal of Macromolecular Science, Part A, 31: 7, 817 — 826

To link to this Article: DOI: 10.1080/10601329409349759

URL: http://dx.doi.org/10.1080/10601329409349759

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J.M.S.—PURE APPL. CHEM., A31(7), pp. 817–826 (1994)

PREPARATION AND PROPERTIES OF ALIPHATIC POLYBENZOXAZOLES FROM 4,4′-DIAMINO-3,3′-DIHYDROXYBIPHENYL AND ALIPHATIC DICARBOXYLIC ACID CHLORIDES BY THE SILYLATION METHOD

KAZUO ITOYA, MICHITOSHI ARATA, MASA-AKI KAKIMOTO,
and YOSHIO IMAI*

Department of Organic and Polymeric Materials
Tokyo Institute of Technology
Meguro-ku, Tokyo 152, Japan

JOUJI MAEDA and TOSHIKAZU KUROSAKI

Department of Industrial Chemistry
Tokyo Institute of Polytechnics
Iiyama, Atsugi-shi, Kanagawa 243-02, Japan

Downloaded At: 16:31 24 January 2011

ABSTRACT

A series of aliphatic polybenzoxazoles of high molecular weights was prepared in three steps by the low-temperature solution polycondensation of tetrakis(trimethylsilyl)-substituted 4,4′-diamino-3,3′-dihydroxybiphenyl with aliphatic diacid chlorides with 7 to 12 methylene units yielding trimethylsilyl-substituted poly(*o*-hydroxyamide) precursor polymers, which were subjected to desilylation with methanol giving the poly(*o*-hydroxyamide)s, followed by thermal cyclodehydration. The aliphatic polybenzoxazoles had melting points in the 172 to 246°C range with glass transition temperatures of 55–97°C. They were stable in the melt state up to 400°C in nitrogen. These polybenzoxazoles and the corresponding bisbenzoxazole model compounds exhibited no liquid crystallinity.

Copyright © 1994 by Marcel Dekker, Inc.

INTRODUCTION

Since the early 1960s, high performance thermally stable polymers have become of major interest to many scientists and industrial technologists [1]. Polybenzoxazoles form a class of such polymers. Although first synthesized three decades ago, aromatic polybenzoxazoles with high rigidity have received relatively little attention until recently [2–5]. Poor solubility and difficult processibility limited these materials as choices for new materials developments. In addition, no systematic studies have been reported on the synthesis and properties of more flexible aliphatic polybenzoxazoles, although there is brief information on them [6].

Polybenzoxazoles were classically synthesized by a two-step method which included the polycondensation of bis(*o*-aminophenol)s with aromatic dicarboxylic acid chlorides giving poly(*o*-hydroxyamide) precursor polymers followed by thermal cyclodehydration [7], and by a one-step process that involved both the melt polycondensation of bis(*o*-aminophenol)s with aromatic diacid diphenyl esters [8] and the solution polycondensation of the bisaminophenol monomers with aromatic dicarboxylic acids in polyphosphoric acid [2, 6]. Recently, a mixture of phosphorus pentoxide and methanesulfonic acid [9] and a mixture of trimethylsilyl polyphosphate and chlorobenzene [10], which acted as both condensing agent and polymerization medium, were used to effect the one-step solution polycondensation. We have developed a new two-step route, silylation method, where trimethylsilyl-substituted bis(*o*-aminophenol)s were employed as monomers in place of the parent bisaminophenol monomers [11].

The purpose of the present investigation is to elucidate the utility of the aliphatic polybenzoxazoles obtained by the two-step procedure from trimethylsilyl-substituted 4,4′-diamino-3,3′-dihydroxybiphenyl and various aliphatic diacid chlorides. There is a report on the synthesis of aliphatic benzobisoxazole compounds, some of which exhibited liquid crystallinity [12]. Hence, a series of aliphatic bisbenzoxazoles were also studied as model compounds for the aliphatic polybenzoxazoles for comparison.

Downloaded At: 16:31 24 January 2011

EXPERIMENTAL

Materials

4,4′-Diamino-3,3′-dihydroxybiphenyl (AHB) was obtained from Wakayama Seika Co., Japan, and used without further purification. 4,4′-Bis(trimethylsilylamino)-3,3′-bis(trimethylsilyloxy)biphenyl (SAHB) was synthesized according to the literature [11] by the reaction of AHB with hexamethyldisilazane and a small amount of trimethylchlorosilane in refluxing toluene. Two distillations under vacuum gave pale yellow solids; bp 195°C/0.5 torr, mp 157°C (literature mp [11] 157–159°C).

Aliphatic carboxylic acids having 7 to 12 alkyl carbon numbers were used as received. Aliphatic dicarboxylic acid chlorides having 7 to 12 methylene units were prepared by the conventional chlorination of the corresponding dicarboxylic acids with thionyl chloride, followed by distillation.

Polyphosphoric acid (PPA) was employed as received. *N*,*N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride.

Synthesis of Model Compounds

In a representative reaction, a flask was charged with 2.16 g (10 mmol) AHB, 2.88 g (20 mmol) octanoic acid, and 30 g PPA. The mixture was heated with stirring at 120°C for 10 hours under a nitrogen atmosphere. The resultant solution was poured into 600 mL water. The precipitate formed was collected, washed successively with aqueous sodium bicarbonate and water, followed by drying under vacuum. The product was further purified by recrystallization from hexane, giving white needles; mp 107°C (by DSC). The yield was 2.25 g (52%). The IR spectrum (KBr) exhibited an absorption band at 1620 cm^{-1} (C=N).

Polymerization

A typical example is as follows: In a flask, 2.53 g (5.0 mmol) SAHB was dissolved in 20 mL DMAc with stirring under nitrogen. The solution was solidified with a dry ice-acetone bath, and to this was added 1.27 g (5.0 mmol) liquid undecanedioyl chloride in one portion. The cooling bath was changed to an ice-water bath, and the mixture was stirred at 0-5°C for 6 hours under nitrogen, giving a viscous solution. Then the polymer solution was poured into methanol. The polymer flakes that precipitated were collected, washed thoroughly with methanol, and dried at room temperature for 12 hours under vacuum. The inherent viscosity of the polymer was 0.43 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30°C. The IR spectrum (film) showed absorptions at 3400 (N—H and O—H) and 1650 cm^{-1} (C=O).

The polymer flakes were placed on a Teflon sheet in a glass oven and heated at 240°C for 30 minutes under vacuum, yielding polybenzoxazole. The IR spectrum (film) exhibited an absorption at 1620 cm^{-1} (C=N).

Analysis. Calculated for $(C_{23}H_{24}N_2O_2)_n$: C, 76.64; H, 6.71; N, 7.77%. Found: C, 76.36; H, 6.49; N, 7.84%.

The other polybenzoxazoles were synthesized by a similar procedure.

Measurements

IR spectra were recorded on a JASCO FT/IR-5000 spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed with Shimadzu thermal analyzers DSC-41M and TGA-40M, respectively. Dynamic thermomechanical analysis (DMA) was carried out with a Toyoseki Reolograph-Solid apparatus.

RESULTS AND DISCUSSION

Model Compound Study

Prior to elucidating the thermal behavior of aliphatic polybenzoxazoles, a series of aliphatic bisbenzoxazoles were synthesized and thermally characterized as the model compounds. The synthesis was effectively carried out by the one-step procedure using PPA from AHB and various aliphatic carboxylic acids (Eq. 1).

Downloaded At: 16:31 24 January 2011

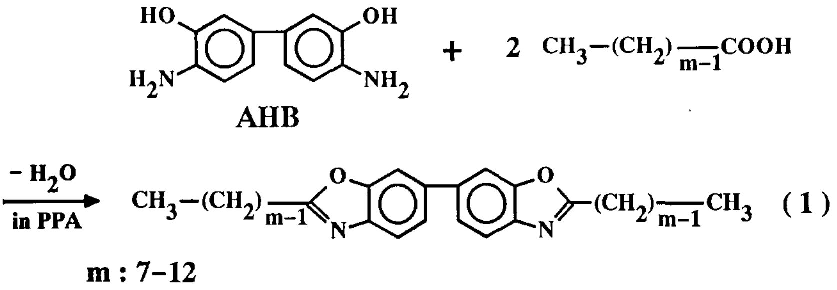


Table 1 summarizes the results of synthesis of the model bisbenzoxazoles; the yield, melting point (mp), freezing point (fp), and elemental analysis. The IR spectroscopy and elemental analysis supported the formation of the bisbenzoxazoles with the proposed structures.

Figure 1 shows two examples of the DSC curves of first heating and cooling cycles for the model bisbenzoxazoles MBO-10 and MBO-11 having 10 and 11 alkyl carbon numbers, respectively. All the model bisbenzoxazoles except MBO-11 exhibited one endothermic peak on heating due to the melting point and one exothermic peak on cooling based on the freezing point, whereas two endothermic peaks on heating were observed for MBO-11 and one sharp exothermic peak on cooling. In

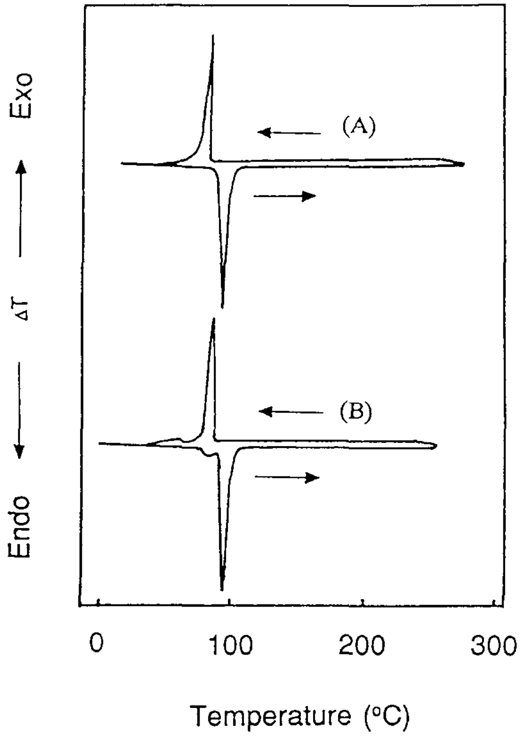


FIG. 1. DSC curves of model bisbenzoxazoles, (A) MBO-10 and (B) MBO-11, at a heating and cooling rate of 10°C/min in air.

Downloaded At: 16:31 24 January 2011

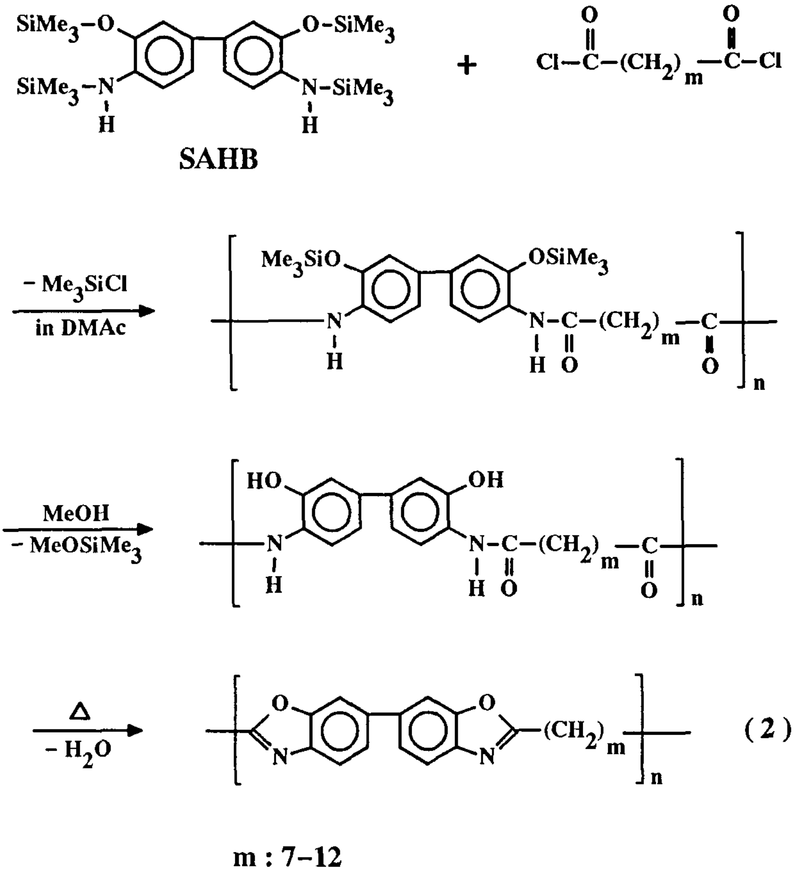
the latter case, no obvious liquid crystalline behavior was observed between the temperatures of the two endothermic peaks. Therefore, all the bisbenzoxazoles, including MBO-11, did not exhibit liquid crystallinity.

As shown in Table 1, the melting points of the model bisbenzoxazoles decreased with increasing carbon numbers of the alkyl group. In addition, the melting points exhibited a well-known odd-even effect. The bisbenzoxazoles having an odd-numbered alkyl group showed higher melting points than those having an even-numbered one.

Polymer Synthesis

Aliphatic polybenzoxazoles could be synthesized by one-step solution polycondensation using PPA. However, removal of the last trace amounts of contaminated phosphate ion in the polymers is rather difficult, and hence the three-step silylation method previously developed [9] was employed here for the preparation of a series of aliphatic polybenzoxazoles. The low-temperature solution polycondensation of SAHB with aliphatic diacid chlorides was carried out in DMAc, yielding the trimethylsilyl-substituted poly(*o*-hydroxyamide) precursor polymers which were subjected to desilylation with methanol, giving the poly(*o*-hydroxyamide)s, followed by thermal cyclodehydration (Eq. 2).

Downloaded At: 16:31 24 January 2011



(2)

TABLE 1. Synthesis and Properties of Model Bisbenzoxazoles

					Elemental analysis, %		
m	Yield, %	mp, °C[a]	fp, °C[a]		C	H	N
7	52	107	95	Calcd	77.74	8.39	6.48
				Found	77.63	8.74	6.42
8	48	93	74	Calcd	78.22	8.75	6.08
				Found	78.09	8.79	6.02
9	59	98	89	Calcd	78.65	9.07	5.73
				Found	78.98	9.37	5.41
10	43	93	83	Calcd	79.03	9.36	5.42
				Found	78.91	9.63	5.41
11	64	78, 94	86	Calcd	79.37	9.62	5.14
				Found	79.64	9.89	5.14
12	89	96	89	Calcd	79.67	9.85	4.89
				Found	79.59	10.18	4.94

[a] Measured by DSC at heating and cooling rates of 10°C/min in nitrogen.

Downloaded At: 16:31 24 January 2011

In the first and second steps, the poly(*o*-hydroxyamide)s having moderate to high inherent viscosities of 0.4–1.1 dL/g were readily obtained in quantitative yields (Table 2). In the next stage the poly(*o*-hydroxyamide)s in the form of flakes were subjected to thermal cyclodehydration at 240°C under vacuum, affording the corresponding aliphatic polybenzoxazoles.

The formation of such polybenzoxazoles was confirmed by means of IR spectroscopy, with the disappearance of absorption bands at 3400 cm^{-1} due to both

TABLE 2. Synthesis and Properties of Aliphatic Polybenzoxazoles

m	η_{inh}, dL/g[a]	T_g, °C[b]	T_m, °C[c]	T_{10}, °C[d]
7	0.92	85	242	455
8	0.93	97	246	460
9	0.43	64	193	460
10	0.87	64	209	460
11	1.12	62	162, 172	465
12	0.86	55	185	460

[a] Measured in poly(*o*-hydroxyamide) at a concentration of 0.5 g/dL in DMAc at 30°C.

[b] Measured by DMA at 10 Hz frequency and a heating rate of 2°C/min in air.

[c] Measured by DSC at a heating rate of 10°C/min in nitrogen.

[d] Temperature of 10% weight loss measured by TG at a heating rate of 20°C/min in nitrogen.

amide N—H and hydroxyl groups and at 1650 cm^{-1} of amide carbonyl for the poly(*o*-hydroxyamide)s, and the appearance of an absorption at 1620 cm^{-1} based on benzoxazole C=N moiety. The elemental analysis also supported the formation of polybenzoxazoles.

Polymer Characterization

All the precursor poly(*o*-hydroxyamide)s were readily soluble in DMAc, and their films could be cast from the DMAc solutions. On the other hand, the aliphatic polybenzoxazoles obtained through thermal cyclodehydration partially dissolved in concentrated sulfuric acid and methanesulfonic acid, and were insoluble in organic solvents.

The thermal behavior of the precursor poly(*o*-hydroxyamide)s and polybenzoxazoles was studied by using DSC, TG, and DMA techniques. Figure 2 shows a typical TG curve for polybenzoxazole PBO-10 having 10 methylene units in nitrogen. This polybenzoxazole, as well as all the other polybenzoxazoles, did not lose weight up to 400°C in nitrogen in the melt state, with a 10% weight loss being recorded at around 460°C.

Figure 3 depicts representative DMA curves, dynamic storage modulus and loss modulus curves, for the polymer film PBO-10. The dynamic loss modulus curve of the polymer exhibited a peak based on the glass transition temperature (T_g) at 64°C, which corresponded well with an inflection point on the dynamic storage modulus curve.

Figure 4 shows two examples of the DSC traces of second heating and cooling cycles for polymers PBO-10 and PBO-11 (having 11 methylene units). In the case of PBO-10, one endothermic peak on heating due to the melting point (T_m) and one

Downloaded At: 16:31 24 January 2011

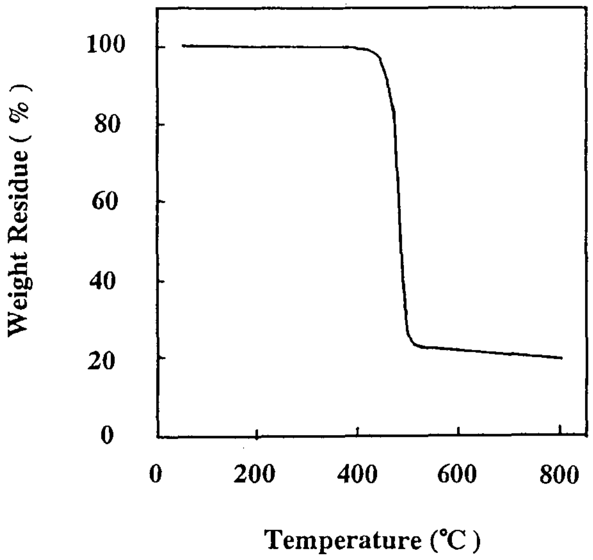


FIG. 2. TG curve of PBO-10 at a heating rate of 20°C/min in nitrogen.

Downloaded At: 16:31 24 January 2011

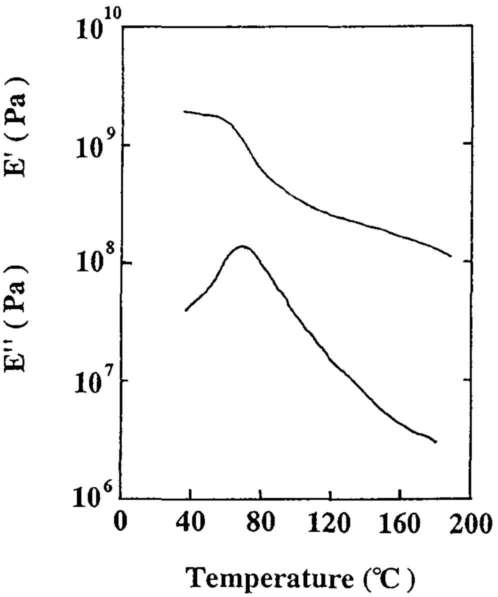


FIG. 3. Temperature dependence curves of dynamic storage modulus E' and dynamic loss modulus curve E'' for PBO-10 film at a frequency of 10 Hz and a heating rate of 2°C/min in air.

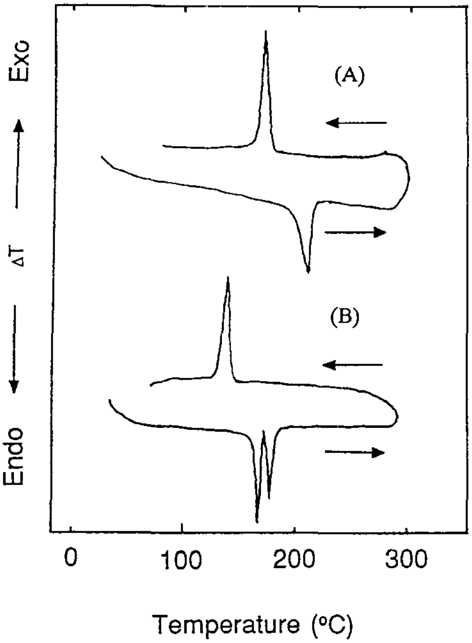


FIG. 4. DSC curves of polybenzoxazoles, (A) PBO-10 and (B) PBO-11, at a heating and cooling rate of 10°C/min in nitrogen.

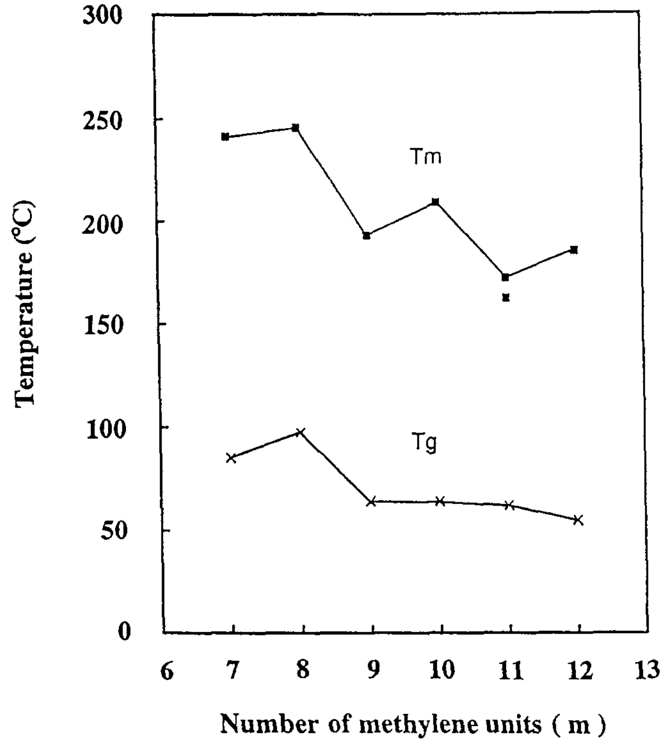


FIG. 5. Effect of number of methylene units on melting point T_m and glass transition temperature T_g of aliphatic polybenzoxazoles.

Downloaded At: 16:31 24 January 2011

exothermic peak based on the freezing point were observed, whereas PBO-11 exhibited two endothermic peaks on heating and one exothermic peak on cooling. The two endothermic peaks of PBO-11 were probably due to recrystallization of metastable crystals, according to the hot-stage polarized microscopic observation. No liquid crystallinity was seen.

Table 2 summarizes the thermal properties of the aliphatic polybenzoxazoles: the T_g, T_m, and decomposition temperature (T_{10}). Figure 5 shows the effect of the number of methylene units on the T_m and T_g values of the aliphatic polybenzoxazoles. The T_m values exhibited a pronounced odd–even effect, while the T_g values did not do so. The polybenzoxazoles having even-numbered methylene units exhibited higher T_m values than the polymers with odd-numbered units. Both of the transition temperatures decrease with an increasing number of methylene units. The decomposition temperatures of the aliphatic polybenzoxazoles were around 460°C in air, indicative of high thermal stability in the melt state.

CONCLUSIONS

A series of aliphatic polybenzoxazoles composed of bisbenzoxazole rings and 7 to 12 methylene units had melting points in the 172 to 246°C temperature range with T_gs of 55–97°C. These polymers were stable in the melt state up to 400°C in nitrogen. Although the aliphatic polybenzoxazoles and the corresponding bisbenzoxazole model compounds exhibited no liquid crystallinity, these polymers might find some applications as new melt processible plastic materials.

REFERENCES

[1] P. E. Cassidy, *Thermally Stable Polymers*, Dekker, New York, 1980.

[2] J. F. Wolfe and F. E. Arnold, *Macromolecules*, *14*, 909 (1981).

[3] E. W. Choe and S. N. Kim, *Ibid.*, *14*, 920 (1981).

[4] S. A. Jenekhe, J. A. Osaheni, J. S. Meth, and H. Vanherzeele, *Chem. Mater.*, *4*, 683 (1992).

[5] N. Ogata, *Makromol. Chem.*, *Macromol. Symp.*, *53*, 191 (1992).

[6] Y. Imai, I. Taoka, K. Uno, and Y. Iwakura, *Makromol. Chem.*, *83*, 167 (1965).

[7] T. Kubota and R. Nakanishi, *J. Polym. Sci.*, *Part B*, *2*, 655 (1964).

[8] W. W. Moyer Jr., C. Cole, and T. Anyos, *J. Polym. Sci.*, *Part A*, *3*, 2107 (1965).

[9] M. Ueda, H. Sugita, and M. Sato, *J. Polym. Sci.*, *Polym. Chem. Ed.*, *24*, 1019 (1986).

[10] B. A. Reinhardt, *Polym. Commun.*, *31*, 453 (1990).

[11] Y. Maruyama, Y. Oishi, M. Kakimoto, and Y. Imai, *Macromolecules*, 21, 2305 (1988).

[12] E. I. Dobrolyubova, A. G. Drushlyak, and A. V. Ivashchenko, *Mol. Cryst. Liq. Cryst.*, *191*, 219 (1990).

Received August 16, 1993
Revision received October 19, 1993

Downloaded At: 16:31 24 January 2011