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The Synthesis, Characterization and Properties of 2, 4, 6-Tris (2-Allylphenoxy) -1, 3, 5-Triazine

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Abstract

2, 4, 6-Tris (2-Allylphenoxy) -1, 3, 5-Triazine with 91% yield was synthesized by reaction of *o*-allylphenol and cyanuric chloride in water in the presence of aq. NaOH at ambient temperature. The product can copolymerise easily with BMI (Bismaleimide) and the copolymer is superior to the homopolymer of BMI in heat resistance and toughness.

Keywords: 2, 4, 6-Tris (2-allylphenoxy) -1, 3, 5-triazine, *o*-allylphenol, cyanuric chloride, bismaleimide(BMI), synthesize, copolymerization.

Introduction

Bismaleimides (BMIs) are widely used as matrix resins for structural composites because of their low cost and ease of processability¹. However, they suffer from inherent brittleness and limited heat resistance. Hence, a popular approach to toughening BMIs is to co-polymerise them with a reactive component. This may take the form of chain extension or a series of intermolecular cycloaddition reactions with alkenyl modifiers². The co-reaction of bis(4-maleimidophenyl) methane with 2,2-bis(3-allyl-hydrophenyl) isopropylidene has been well studied³ and a commercial product, Matrimid 5292 resin, was produced based on these studyings. It is thought that the co-reaction occurs via an "ene/Diels-Alder" mechanism yielding a network which had favorable toughness⁴.

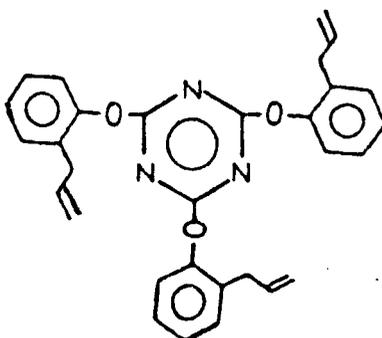
A method to improve the heat resistance of BMIs is to copolymerise them with cyanurate esters⁵. This may form a class of new resins called "BT resins" which have higher heat resistance because of forming of 2,4,6-trisaryloxy-1,3,5-triazine rings in main chain or crosslinking network of copolymers. However, the synthesis of cyanurate esters are more difficult because CNCl (cyanochloride), which has high toxicity, must be used and reaction temperature must be lower (ca. -20°C)⁶. Furthermore, the source of CNCl is limited because of improvement of manufacturing technology of cyanuric chloride⁷.

Cyanuric chloride is an important organic chemical material which is widely used as intermediate to synthesize active dyes⁸, pesticides⁸ and can be used to prepare liner polycyanurate and liner melamine⁹. In particular, several reactive monomers synthesized from cyanuric chloride, such as TAC(trisallyloxy-triazine) and so on, have been used as copolymerization monomers with other monomers or polymers¹⁰. A lot of copolymers have good heat resistance and high adherence to metals.

From the point of view of molecular design, introducing flexible linkage or chains into bismaleimides can effectively improve the toughness of the matrix. On the other hand, introducing of heterocyclic rings into the resins can improve the heat resistance of the cured resins. Allyl is tough and triazine ring is heat resistant, thus, introducing allyl and triazine to bismaleimides can be

obtained a class of matrix which have both of flexibility and thermal stability.

Based on forgoing discussion, we synthesized a reactive monomer, 2,4,6-tris(o-allylphenoxy)-1,3,5-triazine. Scheme 1 depicts the chemical structure of the product. The present work describes an investigation of the synthesis, characterization, thermal and some mechanical behavior of the product.



Scheme 1 Chemical structure of active monomer in this work

Experimental

1. Materials

Allyl chloride and cyanuric chloride were industrial products, and were purified by fractional distilling (b.p 44-45°C) and recrystalling from petroleum ether (60- 90°C), respectively. Phenol was distilled twice. BMI was an industrial product, and was recrystalled twice from toluene before use.

2. Synthesis

2.1 Preparation of allylphenylether (APE) A flask was fitted with a reflux condenser, a dropping funnel and mechanical stirrer. The flask was charged with powder NaOH (48.0g, 1.2mol), n-butanol (400ml). Phenol (94.0g, 1.0mol) dissolved in n-butanol (100ml) was added dropwise to the vigorously stirred mixture under N₂, the temperature rose to 70°C and the mixture turned into transparent. After 0.5h at the temp., allylchloride (92.0g, 1.2mol) was added dropwise over 0.5h to the mixture, and the solution turned into a white slurry. After 4h at 80°C, the mixture was cooled to room temp. and precipitate was separated by flitting. The filtrate was washed with 10% NaOH and water, respectively, dried(MgSO₄), and evaporated. Distillation of the residue (125g) gave a colorless transparent liquid (117.0g, 87% yield; b.p. 93-95°C/ 0.095MPa; n_D 1.5212, Lit¹¹. 1.5200-1.5215). IR. 915,995 cm⁻¹ (allyl group); 1650 cm⁻¹(aryl ring); 1220 cm⁻¹ (-C-O-); 2983 cm⁻¹ (-CH₂)

2.2 Preparation of 2-allylphenol via Claisen arrangement of APE A three-necked flask equipped with a reflux condenser, thermometer and mechanical stirrer was charged allylphenyl ether (100g, 0.745mol). The liquid was heated slowly to boiling under N₂. After several hours at the refluxing temp. Distillation under vacuum gave a colorless transparent liquid with odor(81.0g, 81% yield; b.p 110-113°C/ 0.092MPa; n_D 1.5454, Litt¹¹ 1.5450-1.5455). IR 3482 cm⁻¹ (-OH). 3075, 997, 916 cm⁻¹ (allyl), 1637 cm⁻¹ (aryl ring), 2906, 2976 cm⁻¹ (-CH₂).

2.3 Preparation of 2, 4, 6-Tris (2-allylphenoxy) -1, 3, 5-triazine (TAPT) A three-necked R. B. flask equipped with a dropping funnel, a thermometer and mechanical stirrer was charger with water(300ml), and cyanuric chloride (18.45g, 0.1mol). Then a solution of 2-allylphenol (40.25g,

0.3mol) and NaOH(12.0g, 0.30mol) in 150 ml water saturated by N₂ was added dropwise to the flask with vigorously stirring at certain temperature. After 4h at ambient temp., the solid product (43.5g, 91% yield) was collected by flitting, washing with water and methanol, respectively, and drying. Recrystallization from methanol gave the pure compound (m.p. 108-109°C, Litt¹² 108-109°C) IR 1563,1369 cm⁻¹(triazine ring); 1640 cm⁻¹(aryl ring); 3062, 995, 915 cm⁻¹(allyl); 1175,1117, 1221 cm⁻¹(-C-O-); 2975, 2885 cm⁻¹(-CH₂).

3. Blending, Copolymerization, Flexural and Shear test

A composition of BMI and TAPT (3:1,mol/mol) was first ground in a glass mortar , then thoroughly mixed using a vibrating mixer. The D.S.C traces specimens were obtained thus. The blend then was placed in a 100ml flask and heated at 160±1°Cfor 10 min. in stirring . A brown transparent liquid was obtained. The liquid was poured quickly into an aluminum mould with dimension of 5.8cm×0.86cm×0.62cm, which was placed in an oven at 160°C. The temp. was maintained for 1h and then elevated and kept at 180°Cfor 4h, 200°Cfor 2h, 220°Cfor 5h and 240°Cfor 1h to complete cure. The flexural specimens of blends were obtained thus. Shear specimens was obtained by using the following method: the blend liquid obtained in the flask at 160°Cfor 10 min. was applied on two heated aluminum plates (the dimension of both the plates was 7.02cm×2.02cm ×0.2cm, and applied area of blend liquid was 2.02cm×1.08cm). The aluminum plates were overlapped quickly at the place applied blend and moved to oven to cure by using forging procedure under pressure (1kg/ cm²).

3.1 Measuring of Gel time

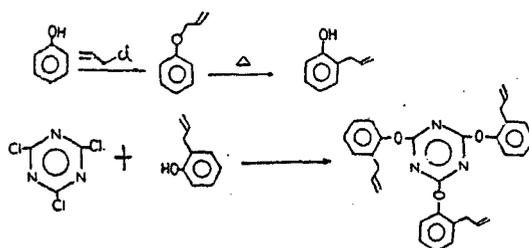
A composition of BMI and TAPT (3:1, mol/mol) was ground in a glass mortar. Thus a blend was obtained. The blend (1.0g) was placed on a constant temp. electrothermal plate and stirred by a thin metal piece. At fixed temp. the period, from the moment the blend was placed on the plate to the moment the blend gelled, was defined as gel time.

4. Characterization

IR spectra were recorded by using Necolex DX4 Spectrometer with KCl pellet. D.S.C traces were recorded using a General V4.1c Dupont 2100. Flexible and Shear strength test were carried out on LT500 test machine.

Results and Discussion

1. Synthesis of TAPT TAPT was prepared according to the procedure depicted in Scheme 2. In this paper we discussed only the synthesis of TAPT by reaction of 2-allylphenol and cyanuric chloride.



Scheme 2 The procedure of synthesis of TAPT in this work

A Japanese patent reported¹² that TAPT was prepared by reaction of 2-allylphenol and cyanuric chloride in acetone in the presence of a trialkylamine such as triethylamine. However, it is more difficult to synthesize TAPT by the method because the synthesis must be in absence of water.

A popular method to synthesize 2,4,6-trisaryloxy-1,3,5-triazine was Dudley's method¹³, i.e. these compounds were prepared by reaction of cyanuric chloride and ArOH in the presence of aq. NaOH in a solution of acetone and water. However, using of Dudley's method cost a lot of acetone.

We synthesized TAPT with high yield in water in the presence of aq. NaOH. Although cyanuric chloride was hydrolyzed easily, forming of 2-allylphenonium ion was very easy in water because of solvolytic role of water. Meanwhile nucleophilicity of the anion was stronger than that of water or OH⁻ due to stabilization effect of allyl group. As a result, forming of TAPT was very quick and yield was higher. It must be pointed out that using of an emulsifier was necessary in synthesis of TAPT in water, because cyanuric chloride is insoluble in water. The emulsifier can make reaction mixture to react completely.

Fig.1 gave IR Spectra of TAPT. Absorption in 1563 and 1369 cm⁻¹ were attributed to triazine ring. Absorption in 915,995cm⁻¹ were attributed to allyl group.

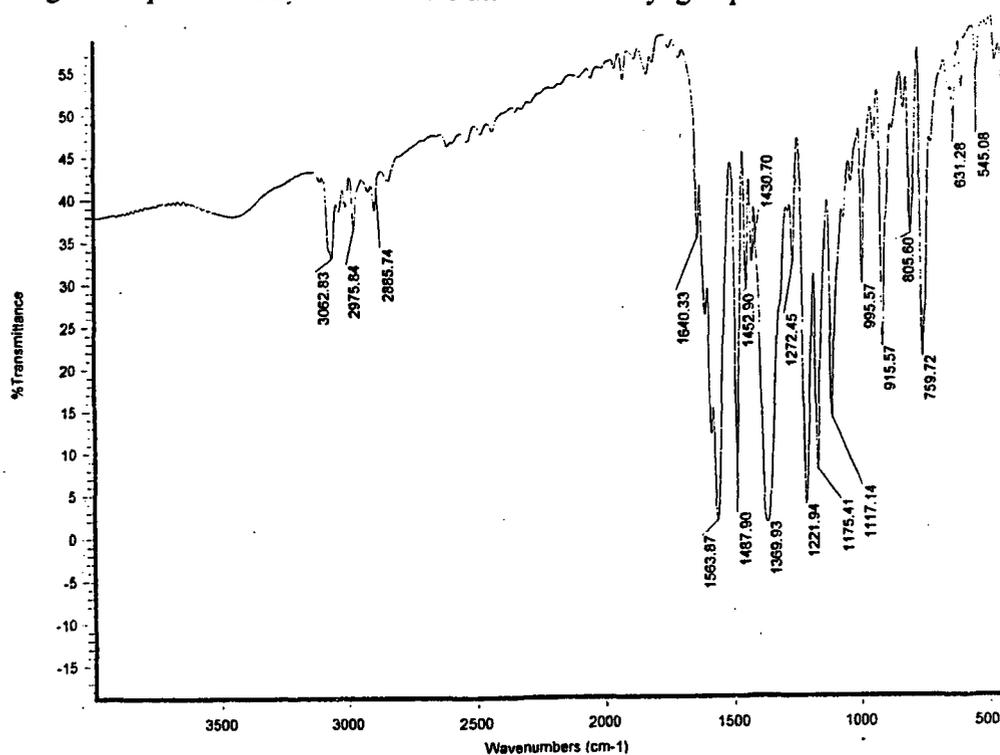


Fig. 1 IR spectra of TAPT

2. Properties of TAPT

2.1 Some physical properties of TAPT

Some physical properties of TAPT was arranged in table 1.

Table 1 Physical properties of TAPT

| appearance | | m.p(°C) | solubility | | | | | | |
|------------|--------|---------|------------|---------|--------------------|-------------------|------------------|-----|-------|
| white | needle | 108-109 | acetone | benzene | CH ₃ OH | CHCl ₃ | CCl ₄ | DMF | ether |
| crystal | | | ○ | ○ | ⊙ | ○ | ○ | ○ | ⊙ |

○ — Soluble; ⊙ — Soluble at heating.

2.2 Study on homopolymerization of TAPT

2.2.1 Thermo-homopolymerization of TAPT

Fig.2 gave D.S.C traces of TAPT. The endothermic peak at 113°C was attributed to melting of TAPT. From 113 to 250 °C, there were not exothermic peak. It showed that homopolymerization of TAPT did not occur in the condition of heating.

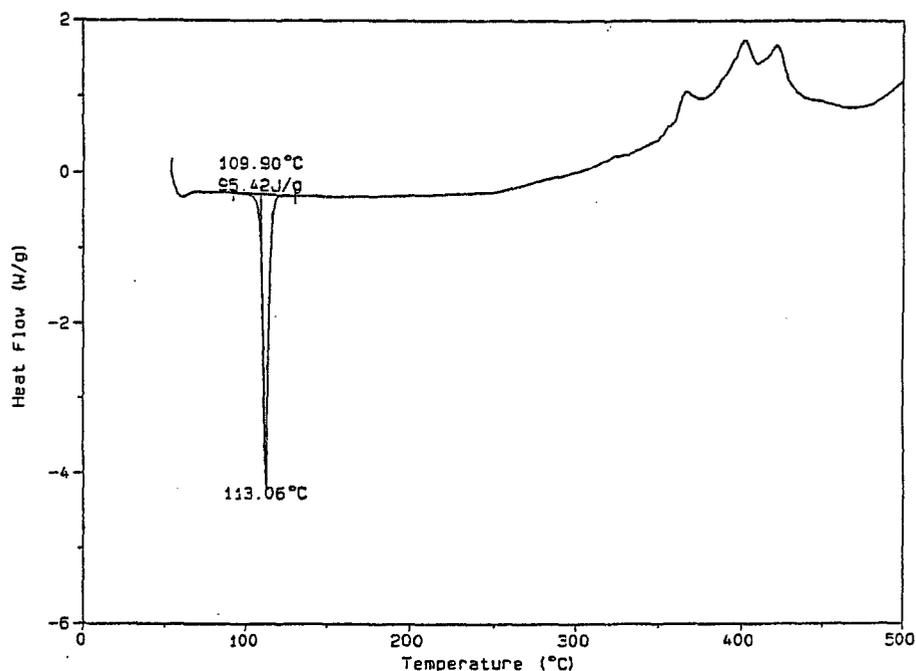


Fig.2 D.S.C traces of TAPT

2.2.2 Homopolymerization of TAPT in the presence of initiator

Homopolymerization of TAPT was investigated in the presence of dicumyl peroxide (DCP). TAPT containing 1% DCP (w/w) was kept temperature at 110°C for 1h and 170°C for 5h under N₂. A sticky brown material which solidified at room temp was obtained. The solid softened and turned to viscous at 70°C. However, it turned to a transparent liquid at ≥ 120°C. It showed that TAPT may homopolymerise in the presence of DCP, but the molecular weight of polymer is lower. Theoretically, homopolymerization of allyl is more difficult because CH₂=CH-CH₂· is very stable. The homopolymerization of TAPT is complicated in the presence of initiators. The effect of type of initiators on the polymerization, weight attributions of the polymer and so on will be investigated in the further works.

2.3 Copolymerization of TAPT with BMI

Figure 3 gave IR spectra of copolymer of TAPT and BMI. It showed that the absorption of allyl group in 915, 995cm⁻¹ had disappeared and triazine ring had been introduced into BMI.

2.3.1 Thermal behavior of copolymer

D.S.C traces of BMI and blend of BMI with TAPT Fig.4 and Fig.5 gave D.S.C traces of BMI and blend of BMI with TAPT (3:1, mol/mol), respectively. It was obvious that the initial exothermal peak temp.of the blend was lower than that of BMI and maximum

exothermal peak temp. of the blend was higher than that of BMI too. This showed that copolymerization of TAPT with BMI improved heat-resistance of BMI and curing temp. of the blend was lower than that of BMI.

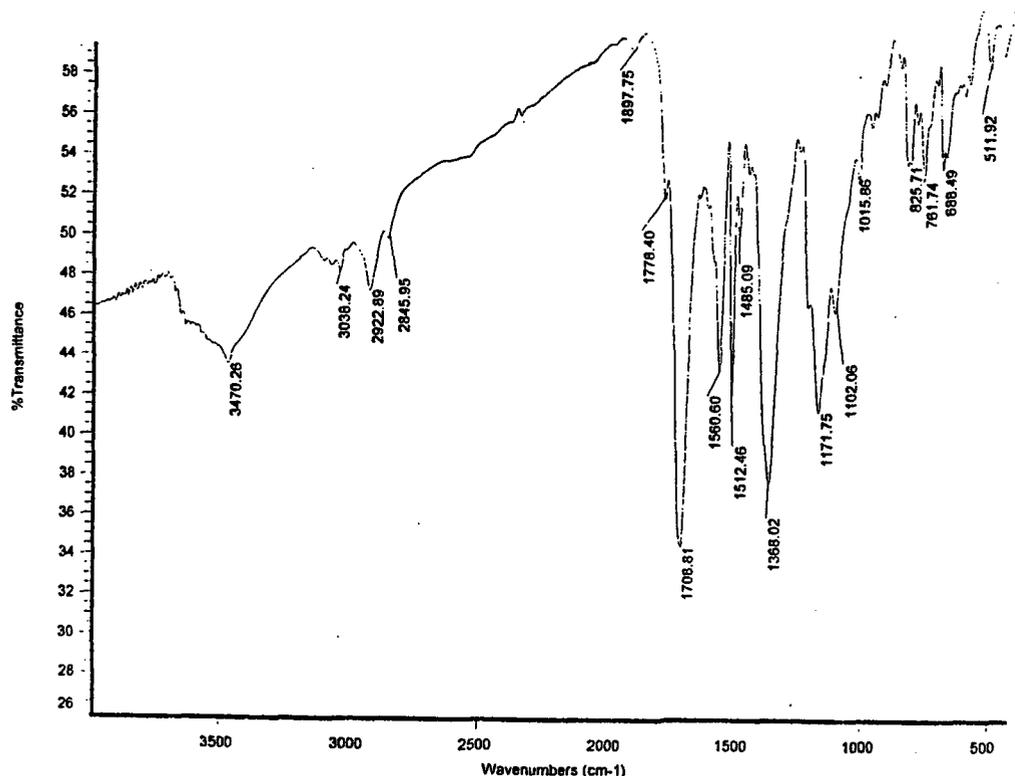


Fig.3 IR spectra of cured copolymer of BMI and TAPT (3:1, mol/mol)

Relationship of Gel time to temperature Table 2 gave the relation of Gel time of BMI and blend of BMI with TAPT to temperature. It showed that adding of TAPT to BMI shortened obviously gel time.

Table 2 Relationship of Gel time of BMI and blend of BMI with TAPT to temperature

| temperature (°C) | Gel time (min.) | |
|------------------|-----------------|-------------------------|
| | BMI | BMI-TAPT (3:1, mol/mol) |
| 160 | — | 55 |
| 180 | 117 | 9.6 |
| 220 | 4.5 | 1.5 |

2.3.2 Some mechanical properties of copolymer

Table 3 gave flexural and shear strength of cured BMI and TAPT-BMI(3:1, mol/mol) at 25 °C. The data showed that TAPT can toughen BMI and copolymer of BMI with TAPT had higher adherence to metal than that of BMI.

Table 3 Flexural and shear strength of BMI and BMI-TAPT at 25°C

| | BMI | BMI-TAPT |
|--|-------|----------|
| Flexural strength (N/mm ²) | 48.30 | 93.74 |
| Shear strength (MPa) | 3.73 | 8.84 |

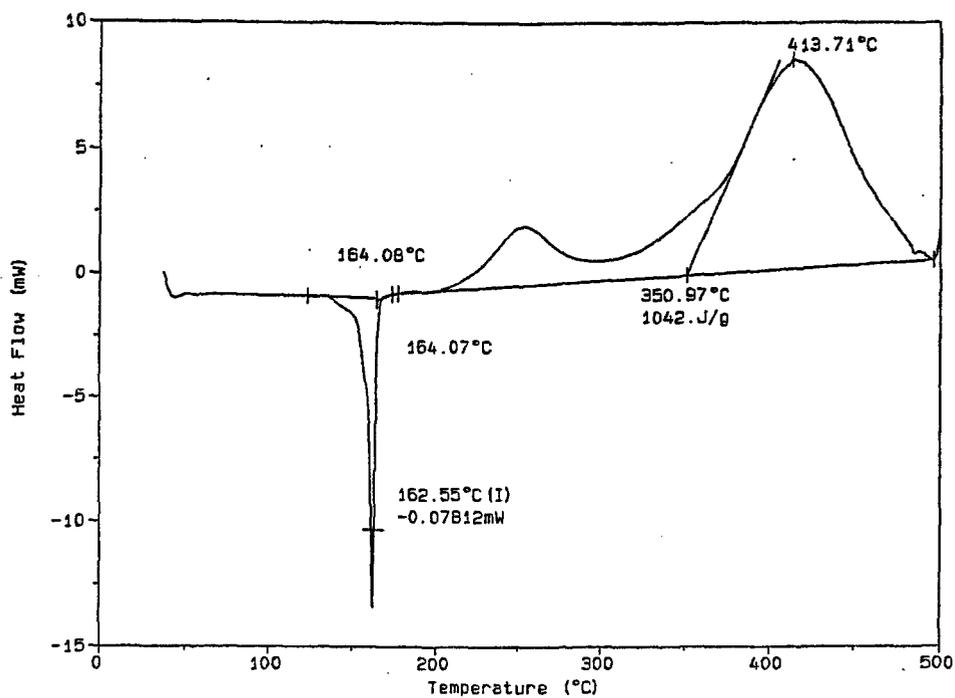


Fig. 4 D.S.C traces of BMI (temperature rate 5°C/min)

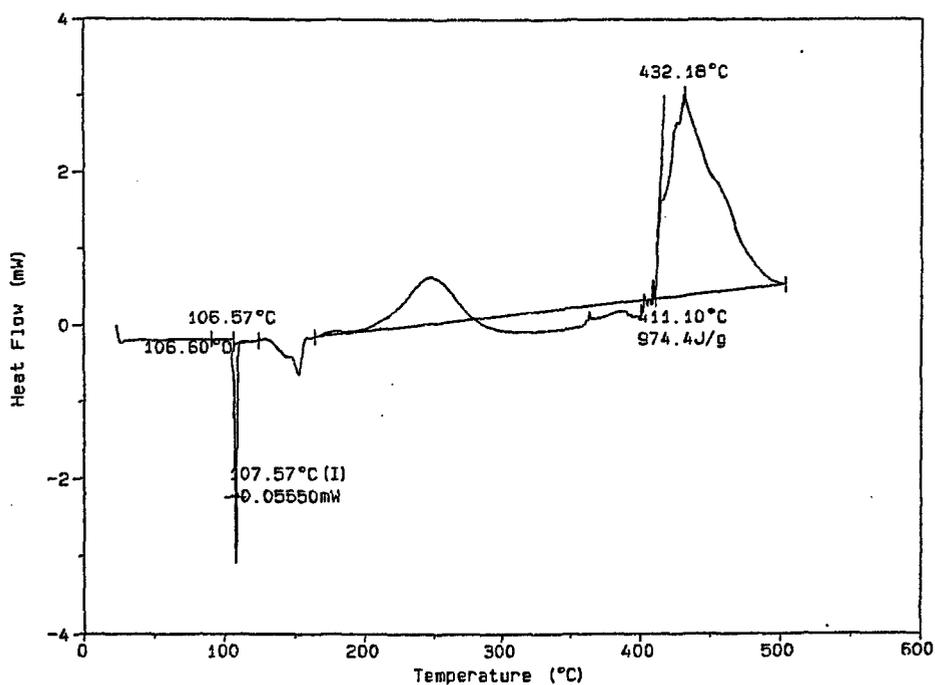
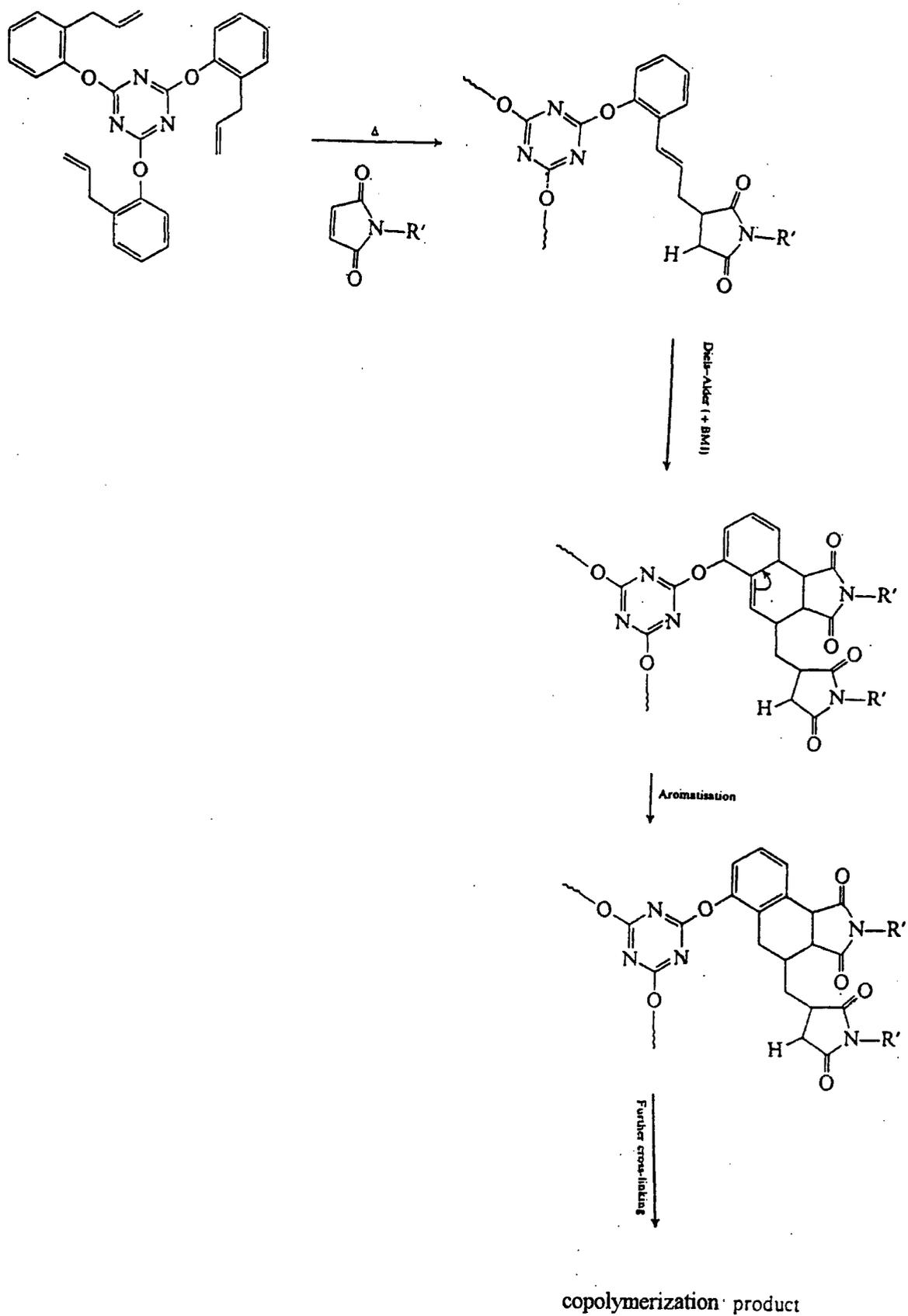


Fig. 5 D.S.C traces of blender of BMI and TAPT (temperature rate 5°C/min)

Copolymerization of TAPT and BMI



Main Results

1. TAPT was synthesized with higher yield in water;
2. Heat resistance and toughness of copolymer of BMI with TAPT were higher than these of BMI.

Reference and Note

- 1 R.Chandra and L. Rajabi, J.M.S.—*Rew.Macromol. Chem. Phys.*, C37(1), 61-96 (1997)
- 2 Crivello. J.V. *J. Polym. Sci.: Polym. Chem. Ed.* 11.(1973) 1185
- 3 Zahir, Sheik, A.C. Chaudhari. M.A. and King , J. *Makromol. Chem. Macromol Symp.* 25 (1989)141
- 4 Barto, J. M, Greenfield, D.C. L, Hamerton, I. And Jones, J. R, *Polym. Bull.* 25 (1991) 475
- 5 Moro Gaku, *ASC Polymer Material Science and Engineering* 621 (71), 1994
- 6 E. Grigat, *ibid*,551 (71),1994
- 7 Private letters
- 8 Chen Lube et.al: “Active dyes” (Chinese), Chemical Industry Press (1991)
- 9 G. Allen and A.G. De Boos, *Polymer* , V.15, 56-59 (1974)
- 10 I.K. Varma, S.P. Gupta and D.S. Varma, *J.Appli. Polym, Sci.* V33, 151-164 (1987)
- 11 Adams. R. edited “Organic Reactions”, Wiley Co. 1954.P27
- 12 Japan Kokai 52136298(1977)
- 13 J.R.Dudley, J.T.Thurston, F.C. Schaefer, D. Holm-Hansen, C.J.Hull and P. Adans, *J.Amer. Chem. Soc.* 73, 2986(1951)