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A new hyperbranched polymer with polar chromophores for nonlinear optics

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A new three-dimensional hyperbranched polymer with 4-(2-cyano-2-methoxy-carbonylvinyl)aniline as a second-order nonlinear optical chromophore has been synthesized starting from 4-formyl-*N*,*N*-di(2-hydroxyethyl)aniline and cyanoacetic acid by a one-pot Knoevenagel polycondensation using 4-(dimethylamino)pyridine as a base. This hyperbranched polymer with a good solubility in polar organic solvents, such as *N*,*N*-dimethylformamide and methyl sulfoxide, was characterized by ^{1}H n.m.r., i.r. and u.v.-vis spectroscopies. Differential scanning calorimeter analysis showed that this polymer exhibited a glass transition temperature at 86°C. The second-harmonic generation signal has been observed from the poled films of this hyperbranched polymer. © 1997 Elsevier Science Ltd.

(Keywords: hyperbranched polymer; one-pot Knoevenagel polycondensation; nonlinear optical materials)

INTRODUCTION

The development of polymers with new chemical structures for nonlinear optical (NLO) materials is an extremely active field. To date, most NLO polymer research has focused on several types of one-dimensional nonlinear optical polymers, such as side-chain polymers (as shown in *Figure 1a*) and main-chain polymers in which NLO chromophores can be aligned as a shoulder-to-shoulder, a head-to-tail, a head-to-head, and a random style (*Figures 1b, c, d, e*)[1–10]. In order to develop new three-dimensional polymers for nonlinear optics, a hyperbranched polymeric structure was selected as a novel NLO material design. It is well known that hyperbranched polymers with three-dimensional structure are highly branched non-cross-linked polymers synthesized from AB_n monomers where n should be larger than 1. Such materials were first described by Flory[11], but only in recent years has purposeful synthesis and characterization of this class of polymers been undertaken[12–20] and attracted increasing attention due to the expectation that their unique spherical structure will impart unusual properties[21]. Recently, hyperbranched polymers and dendrimers with carbazole NLO chromophores have been synthesized in our laboratory[22–24]. Some of our research work on these materials indicated that such three-dimensional organic NLO materials have good reasonable NLO properties.

We report the synthesis and characterization of a new hyperbranched polyester containing 4-(2-cyano-2-methoxycarbonyl)aniline as a polar NLO chromophore. In this hyperbranched polymer, the chromophores were linked at the cross positions of the branches (as shown in *Figure 1f*). Each branch chain looks like a head-to-tail main-chain backbone[3,4,25].

EXPERIMENTAL

Synthesis of N,N-*di(2-acetoxyethyl)aniline (3)*

A mixture of 25 g (138 mmol) *N*,*N*-di(2-hydroxyethyl)-aniline, 50 ml acetic anhydride and 4 ml triethylamine was kept at room temperature for 24 h. To the reaction mixture 300 ml water was added under stirring. After 8 h, the solution was extracted three times with ether, and the ether extract washed three times with 15% Na_2CO_3 and three times with water. After removal of the solvent, *N*,*N*-di(2-acetoxyethyl)aniline was obtained in 94% yield (33.2 g) as a colourless oil. ^{1}H n.m.r. ($CDCl_3$, TMS, ppm): 2.05 (*s*, 6H, 2 × $-CH_3$), 3.62 (*t*, 4H, $J = 6.27$ Hz, 2 × $-OCH_2-$), 4.24 (*t*, 4H, $J = 6.27$ Hz, 2 × $-NCH_2-$), 6.74 (*m*, 3H, H_{be}), 7.23 (*m*, 2H, H_{be}).

*Synthesis of 4-formyl-*N,N-*di(2-acetoxyethyl)aniline (4)*

To 11.4 g (156 mmol) DMF was added 24 g (156 mmol) $POCl_3$ in 90 min at 0°C. After the reaction mixture warmed to room temperature, 20 g (78 mmol) *N*,*N*-di(2-acetoxyethyl)aniline in 50 ml of 1,2-dichloroethane was added. The mixture was refluxed for 6 h and cooled to room temperature. The reaction mixture was added to 500 ml of water. The mixed solution was extracted three times with chloroform. After removal of solvent under reduced pressure, the crude sample was purified by chromoatography on a silica gel column to give 18 g (78.8%) of product as colourless oil. ^{1}H n.m.r. ($CDCl_3$, TMS, ppm): 2.01 (*s*, 6H, 2×$-CH_3$), 3.69 (*t*, 4H, $J = 6.27$ Hz, 2×$-OCH_2-$), 4.23 (*t*, 4H, $J = 6.27$ Hz, 2× $-NCH_2-$), 6.79 (*d*, 2H, $J = 8.91$ Hz, H_{be}), 7.71 (d, 2H, $J = 8.91$ Hz, H_{bz}), 9.72 (s, 1H, -CHO).

*Synthesis of 4-formyl-*N,N-*di(2-hydroxyethyl)aniline (5)*

To 12 g (41 mmol) 4-formyl-*N*,*N*-di(2-acetoxyethyl) aniline in 100 ml ethanol was added 8 g (200 mmol) sodium hydroxide in 10 ml water. After reaction was

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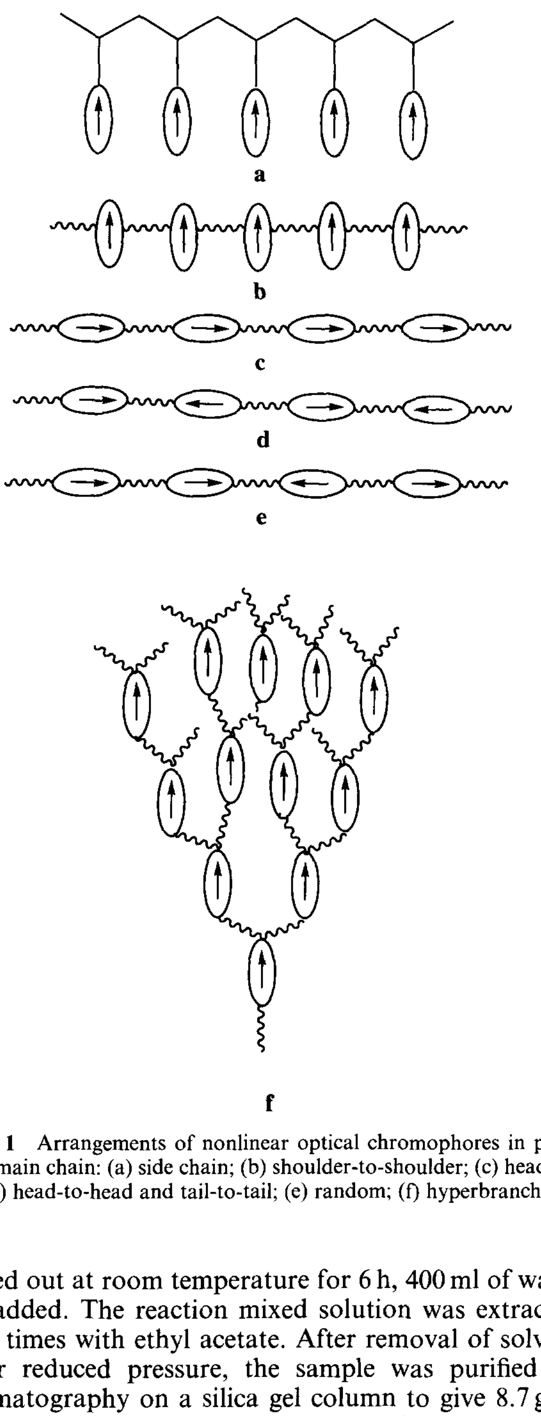


Figure 1 Arrangements of nonlinear optical chromophores in polymeric main chain: (a) side chain; (b) shoulder-to-shoulder; (c) head-to-tail; (d) head-to-head and tail-to-tail; (e) random; (f) hyperbranched

carried out at room temperature for 6 h, 400 ml of water was added. The reaction mixed solution was extracted three times with ethyl acetate. After removal of solvent under reduced pressure, the sample was purified by chromatography on a silica gel column to give 8.7 g of product, which was recrystallized from dichloromethane/hexane. Elemental analysis: calculated for $C_{11}H_{15}NO_3$: C, 63.16; H, 7.18; N, 6.70%. Found: C, 63.28; H, 7.05; N, 6.57%. ^{1}H n.m.r. ($CDCl_3$, TMS, ppm): 3.69 (*t*, 4H, $J = 5.95$ Hz, 2×-OCH_2-), 3.90 (*t*, 4H, $J = 5.95$ Hz, 2×-NCH_2-), 3.92 (*s*, 2H, 2×-OH), 6.69 (*d*, 2H, $J = 8.91$ Hz, H_{be}), 7.66 (*d*, 2H, $J = 8.91$ Hz, H_{bc}), 9.65 (*s*, 1H, -CHO). I.r. (KBr): 3478 (OH), 3032 (aromatic), 2943 (aliphatic), 1685 (C=O), 1608, 1550, 1520 (aromatic), 1404, 1350, 1319, 1248, 1178, 1047, 817 cm^{-1}.

Synthesis of hyperbranched polymer (6)

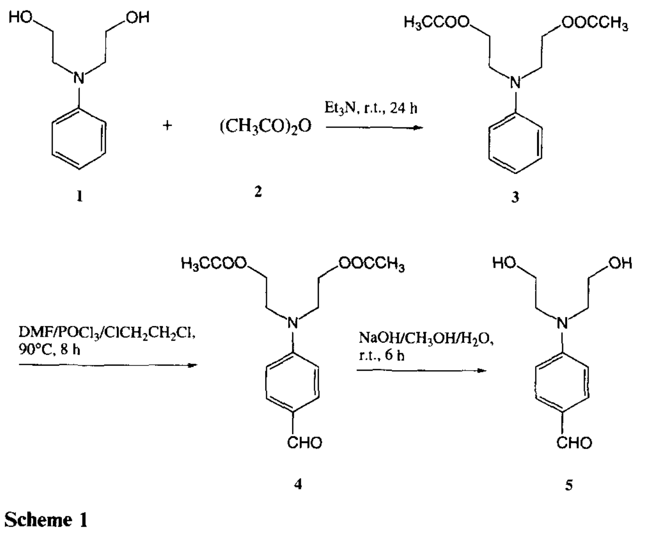
To 1 g (4.78 mmol) 4-formyl-*N*,*N*-di(2-hydroxyethyl) aniline and 0.85 g (10 mmol) cyanoacetic acid in 20 ml anhydrous tetrahydrofuran (THF) at 5°C was added 2.1 g (10.2 mmol) *N*,*N*′-dicylohexylcarbodiimide (DCC). After the reaction mixture was kept at 5°C for 2 h, t.l.c. analysis showed that the esterfication reaction was finished. The THF solution was then filtered from dicyclohexylurea. To this THF solution at room temperature was added 0.8 g (6.56 mmol) of DMAP. The polycondensation reaction was carried out in THF for 30 min, then organic solvent was removed by a nitrogen purge. The polycondensation was kept in the solid state for 2 h under nitrogen purge. The polymer was dissolved in DMF and purified by reprcipitation into methanol three times from DMF. The polymer prepared was dried under vacuum at room temperature for 48 h; yield 0.87 g. I.r. (KBr): 3033 (aromatic), 2955 (aliphatic), 2216 (CN), 1747 (C=O), 1711 (C=O), 1610, 1570, 1516 (aromatic), 1386, 1331, 1275, 1234, 1178, 1138, 1093, 1005, 933, 825, 760 cm^{-1}.

Measurements

I.r. spectra were recorded on a Shimadzu FTIR-4100 spectrophotometer. U.v-vis spectra were recorded with a Shimaduz UV-3100 spectrophotometer. ^{1}H n.m.r. spectra were obtained using a J JNM-EX270 spectrometer operating at 270 MHz in $CDCl_3$. Chemical shifts are in parts per million from internal tetramethylsilane. Thermal analysis was conducted on a Perkin-Elmer DSC-7 instrument at a heating rate of 10°C min^{-1}. The T_g was taken as the midpoint of the heat capacity change. Thermal gravimetric analyses were performed on a Perkin-Elmer TGA-7 at a heating rate of 10°C min^{-1}. The solution viscosity of the polymer was measured on an Ubelhode viscometer in DMSO solution (0.2 g dl^{-1}) at 30°C. Elemental analyses were performed on a Riken Microanalytical Laboratory.

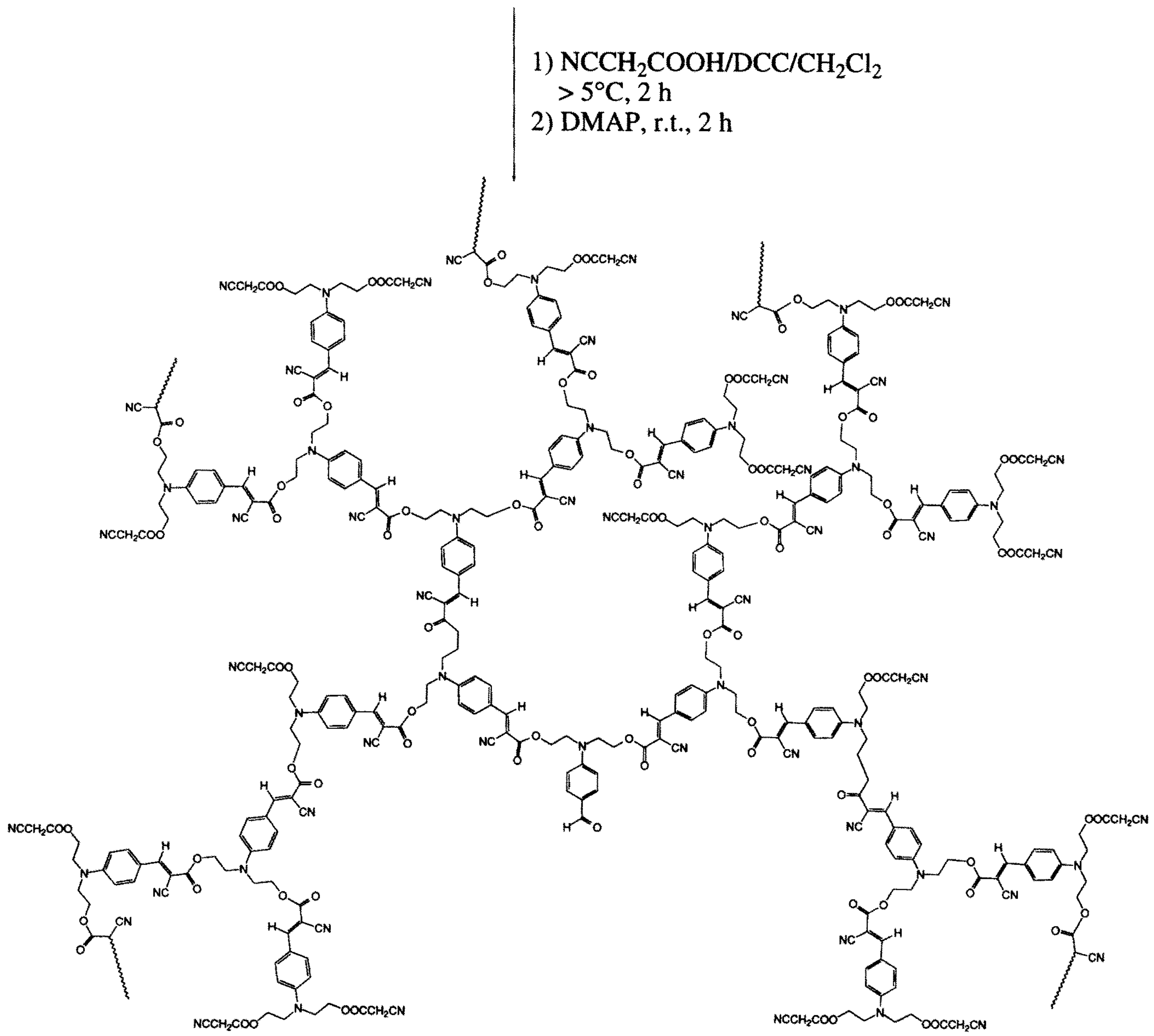
RESULTS AND DISCUSSION

Schemes 1 and *2* show the synthetic route to hyperbranched polymer **6**. *N*,*N*-Di(2-hydroxyethyl)aniline (**1**) reacted with acetic anhydride yielded *N*,*N*-di(2-acetoxyethyl)aniline (**3**) in the presence of triethylamine. Compound **3** reacted with phosphorus oxychloride ($POCl_3$)/dimethylformamide (DMF) to afford 4-formyl-*N*,*N*-di(2-acetoxyethyl)aniline (**4**), which was purified by a column chromatography. 4-Formyl-*N*,*N*-di(2-hydroxyethyl)aniline (**5**) could be obtained by the treatment of compound **4** with aqueous NaOH in ethanol. Hyperbranched polymer **6** was synthesized



Scheme 1

5



1) $NCCH_2COOH/DCC/CH_2Cl_2$
$> 5°C$, 2 h
2) DMAP, r.t., 2 h

6

Scheme 2

from **5** in a one-pot reaction by Knoevenagel polycondensation. Esterification of **5** with cyanoacetic acid in tetrahydrofuran (THF) solution using *N,N*-dicylohexylcarbodiimide (DCC) as a water acceptor. After a check by thin layer chromatography (t.l.c.) showed that the esterification reaction was finished, 4-(dimethylamino)-pyridine (DMAP) was added as a base. After the THF was removed by a nitrogen purge, the polycondensation was kept in solid state for 2 h to give the hyperbranched polymer **6** in high yield.

This hyperbranched polymer obtained as a yellow solid is soluble in polar organic solvent, such as DMF and methyl sulfoxide (DMSO). Thin films of the polymer could be obtained from its hot DMF solution by a spin-coating technique. *Figure 2* shows the u.v.-vis absorption spectrum of the polymer film of about 0.1 μm thickness. The absorption maximum (λ_{max}) of the chromophore, 4-(2-cyano-2-methoxycarbonylvinyl)aniline, was observed at 405 nm in the u.v.-vis spectrum. However, the absorption due to core terminal group, 4-formylaniline, could not be observed. There is only one core terminal group available in one hyperbranched polymeric molecule. If the molecular weight of the hyperbranched polymer was large, the ratio of the core terminal group would be small. It should be difficult to find the signal of the absorption based on the core terminal group.

Figure 3 shows the ^1H n.m.r. spectrum of the hyperbranched polymer **6**, in which the assignments are generally consistent with the structure drawn. The chemical shifts of the methylene groups in the terminal group ($-NCH_2CH_2OOC-CH_2CN$) appear at 4.33 ppm ($-NCH_2-$), 4.00 ppm ($-CH_2CN$) and 3.83 ppm ($-CH_2O-$),

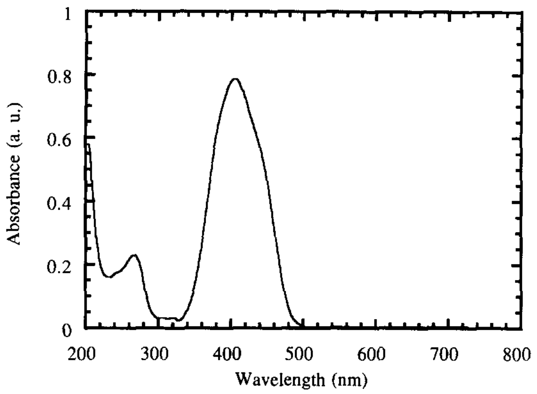


Figure 2 U.v.-vis spectrum of the hyperbranched polymer **6** in thin film

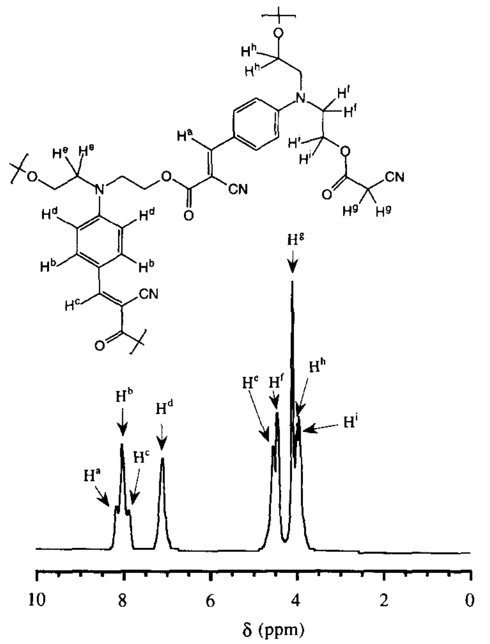


Figure 3 ^{1}H n.m.r. spectrum of the hyperbranched polymer **6** in DMSO

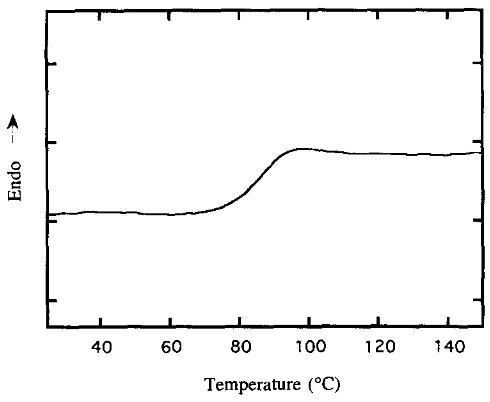


Figure 4 D.s.c. trace of the hyperbranched polymer **6**

respectively. The chemical shifts due to the methylene protons of -$NCH_2CH_2OOC(CN)C{=}C$) appear at 4.43 ppm (-NCH_2-) and 3.88 ppm (-CH_2O-). The chemical shifts of vinyl proton (-$HC{=}C(CN)$-) appear at 7.76 and 8.07 ppm. These two chemical shifts are due to the existence of two kinds of chromophore conformations. The chemical shift due to formyl group (CHO) of the core terminal group cannot be found in the ^{1}H n.m.r. spectrum. This result also suggests that the ratio of the core terminal group is very small in this hyperbranched polymer. The assignments of all chemical shifts according to the expected structure are indicated in *Figure 3*.

The i.r. spectrum of the hyperbranched polymer **6** shows absorption due to a cyano group which can be observed at around 2216 cm^{-1}. Absorption for two kinds of the carbonyl groups appear at 1747 and 1711 cm^{-1}, respectively.

Differential scanning calorimeter (d.s.c.) measurement showed no crystalline transitions for this hyperbranched polymer. *Figure 4* shows a d.s.c. trace of the polymer from which the glass transition temperature (T_g) can be deduced. It is found that the T_g of the hyperbranched polymer **6** is about 86°C. Thermal stability of the hyperbranched polymer **6** was studied by thermal gravimetric analysis (t.g.a.). The hyperbranched polymer appears to be stable in air up to a temperature of about 330°C.

The viscosity ($\eta_{inh} = 0.27$ dl g^{-1}) of the hyperbranched polymer **6** was obtained from DMSO solution at 30°C. According to work on the relationship between the viscosity η and the molecular weight of the hyperbranched polyesters reported by Turner *et al.*[26], the molecular weight for hyperbranched polyesters with $\eta_{inh} = 0.27$ dl g^{-1} ranges from 10 000 to 100 000. Although a direct comparison of the viscosity of the hyperbranched polymer **6** with that of hyperbranched polyester is not strictly valid, a comparison of their physical properties is reasonable. The value of this viscosity suggests that the molecular weight of the hyperbranched polymer **6** should be large.

The orientation of chromophores in the polymeric thin films monitored by second harmonic generation (s.h.g.) could be achieved by the corona poling (7.5 kV) at about 120°C. The s.h.g. measurements were performed using a polarized Q-switched Nd-YAG laser beam ($\lambda = 1064$ nm). A Y-cut quartz crystal plate was used as a reference. The second harmonic (s.h.) intensity was measured using the standard Maker fringe technique[27]. The s.h.g. signal was observed from these poled films of the hyperbranched polymer **6**. However, the s.h. coefficient (d_{33}) was not large. This was probably caused by the difficulty in alignment of the NLO chromophores which are at the cross positions of the

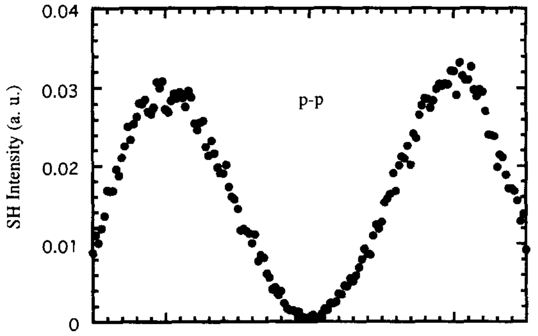


Figure 5 S.h. intensity vs incidence angle for a poled film of the hyperbranched polymer **6** with 0.23 μm thickness

branches, like the head-to-tail polymers[28]. In this hyperbranched polymer, each branch chain looks like a head-to-tail main-chain. Poling behaviour of this type of hyperbranched polymer should be similar to the head-to-tail polymer. The d_{33} could be estimated from the angular dependence of the s.h. intensity using the formula given by Hayden[29]. *Figure 5* shows a typical relation between the s.h. intensity and the incidence angle. A Y-cut quartz plate ($d_{11} = 0.5\,\mathrm{pmV}^{-1}$) was used as a reference material. Preliminary results of the s.h.g. studies indicated that the value of d_{33} for the hyperbranched polymer **6** was about $2.8\,\mathrm{pmV}^{-1}$. Further studies and results on the synthesis and nonlinear optical properties of the hyperbranched polymers with NLO chromophores at side position of the branches will be forthcoming.

CONCLUSIONS

A hyperbranched polymer containing a polar chromophore, 4-(2-cyano-2-methoxycarbonylvinyl)aniline, has been synthesized in a one-pot reaction from 4-formyl-*N*,*N*-di(2-hydroxyethyl)aniline by Knoevenagel polycondensation using DMAP as a base catalyst. The spectroscopies of the polymers were in good agreement with the proposed structure. Detailed studies on the NLO properties of this type of polymer are now underway.

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