PII: S0032-3861(97)10003-9S0032-3861(97)10323-8

Polymer Vol. 39 No. 15, pp. 3551–3558, 1998

0032-3861/98/$19.00+0.00

Polymers from coumarines: 4. Design and synthesis of novel hyperbranched and comb-like coumarin-containing polymers

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(Received 8 July 1997)

Novel monomers containing coumarin groups [2-(7-Cumarinyloxy)0ethoxy]dimethyl terephthalate and [6-(3-carboxy)coumarinyl] diacetylhydroquinone were synthesized and polymerized by high temperature polycondensation to give hyperbranched and comb-like coumarin-containing polymers. All polymers were completely soluble in chlorinated aliphatic hydrocarbons and showed M_n in the range of 2000–50 000 and gave film of good optical quality on casting from solution. All polymers except one were amorphous with T_g in the range of 100–230°C and thermostability of 370–415°C. All polymers were found to be blue emitters emitting light in the range 450–492 nm. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: hyperbranched polymers; coumarin; polyesters)

INTRODUCTION

Coumarines (2H-1-benzopyran-2-ones) have been recently paid much attention for their fluorescent properties and physiological activities. They are widely used as laser dyes[1,2] due to their high photostability and quantum yield of photoluminescence, The chemical modification of coumarines allows us to vary emission wavelength continuously throughout the visible spectrum[3]. Coumarines were also found to be electroluminescent. Thus, a dispersion of coumarin **6** in polymethylmethacrylate showed electroluminescence peaking at 554 nm[4].

Although many papers have been published on the synthesis of coumarines and various reviews are available[3,5] very little attention has been paid to the incorporation of coumarines into polymers, and furthermore none of the papers[6–12] on coumarin-containing polymers dealt with the optical properties. The studies were mainly focused on physiological activities of coumarin-containing polymers. On the other hand, as far as electroluminescence (EL) is concerned, polymeric materials containing coumarin emitter units have the advantage over low molecular weight analogies, especially in making EL devices, due to the absence of phase separation and the possibilities of thin films preparation with good optical quality by simple casting.

A series of novel coumarin-containing monomers and polymers has recently been synthesized and characterized by the authors. Among them were polyamides derived from 6-ethynylphenyl coumarin dicarboxylic acid and aliphatic diamines[13], polyesters based on 6-(3′-hydroxy)-phenylcoumarin-3-carboxylic acid and 6,6′-biscoumarinyl-3,3′-dicarboxylic acid[14], and polynorbornene bearing 7-substituted coumarin in the side chain[15]. All polymers showed photo- and EL properties, however, polyamides and polynorbornene presented difficulties in fabrication of EL devices; thus polynorbornene tended to cross-link on standing, while the solvent trapped in polyamides destroyed the EL device. Polyesters containing 6-phenylcoumarin and 6,6′-biscoumarinyl groups showed good emission properties with reasonable solubility in volatile solvents like chloroform. Bearing in mind that coumarin-containing polyesters presented the best combination of processability and emission properties the present authors aim to develop synthetic approaches to comb-like and hyperbranched coumarin-containing polyesters with better processability. This paper describes the synthesis and characterization of novel polyesters with lateral 7-oxycoumarin group as well as hyperbranched coumarin-containing polymers based on 6-phenylcoumarin derivatives.

EXPERIMENTAL

Materials

Benzoquinone was purified by sublimation. Ethylene glycol was distilled under reduced pressure, decanediol was recrystallized from hexane. Hydroxydimethyl terephthalate (**3**) and 6-aminocoumarin-3-carboxylic acid (**9**) were prepared according to the literature[16,14] as shown in *Scheme 1*.

7-(2-chloroethoxy)coumarin (**5**). A solution of 7-hydroxycoumarin (**4**) (3.0 g, 18.5 mmol), 1,2-dichloroethane (10 g 101 mmol) in *N*-methylpyrrolidone (NMP) (40 ml) was stirred at 60°C for 4 h in the presence of K_2CO_3 (2.6 g, 18.8 mmol). The reaction mixture was poured into 5% HCl, the precipitate formed was filtered off and crystallized from ethanol. Yield 60%. Mp = 121–122°C. IR (cm^{-1}) 3076 (CH arom), 2968 (CH aliph), 1736 (C=O ester), 1612 (C=C arom). ^{1}H-n.m.r. ($CDCl_3$) 7.62 (d, 1H,

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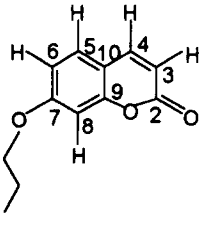
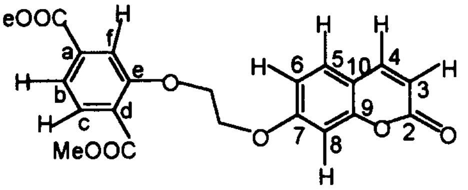
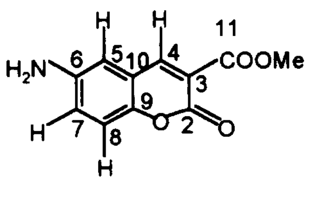
$J = 9.6$ Hz, H^4), 7.38 (d, 1H, $J = 8.4$ Hz, H_5), 6.87 (d,d, 1H, $J_1 = 8.4$ Hz, $J_2 = 2.4$ Hz, H^6), 6.81 (d, 1H, $J = 2.4$ Hz, H^8), 6.28 (d, 1H, $J = 9.6$ Hz, H^3), 4.29 (t, 2H, $J = 5.7$ Hz, —CH_2O—), 3.85 (t, 2H, $J = 5.7$ Hz, —CH_2Cl). ^{13}C-n.m.r. 161.4 (C^2), 161.0 (C^7), 155.9 (C^9), 143.2 (C^4), 129.0 (C^5), 113.7, 112.9, (C^6, C^3), 113.1 (C^{10}), 101.8 (C^8).



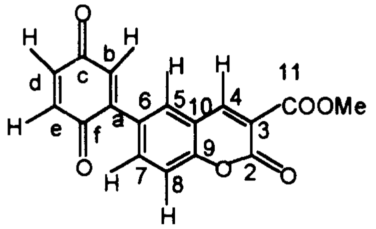
[2-(7-cumarinyloxy)ethoxy]dimethyl terephthalate (**6**). A solution of compound **5** (1.8 g, 8.0 mmol), compound **3** (1.7 g, 8.1 mmol) in NMP (20 ml) was stirred at 70°C for 24 h in the presence of K_2CO_3 (1.2 g, 8.7 mmol). The reaction mixture was poured into 200 ml of 5% HCl. The precipitate formed was filtered off and crystallized from ethanol. Yield 55%. Mp = 147°C. IR (cm^{-1}) 3084 (CH arom), 2957 (CH, aliph) 1720 (C=O, ester), 1618, 1574 (C=C arom), ^{1}H-n.m.r., ($CDCl_3$) 7.81 (d, 1H, $J = 9.4$ Hz, H^c), 7.72 (d, 1H, $J = 1.2$ Hz, H^f), 7.68 (d,d, 1H, $J_1 = 9.4$ Hz, $J_2 = 1.2$ Hz, H^b), 7.62 (d, 1H, $J = 9.4$ Hz, H^4), 7.38 (d, 1H, $J = 8.7$ Hz, H^5), 6.92 (m, 1H, H^6), 6.89 (s, 1H, H^8), 6.27 (d, 1H $J = 9.4$ Hz, H^3), 4.50–4.45 (m, 4H, $(CH_2)_2$), 3.95 (s, 3H, Me *metha* to C^e), 3.86 (s, 3H, Me *ortho* to C^e). ^{13}C-n.m.r. 166.0 (2 COOMe), 161.8 (C^2), 161.0 (C^7), 158.1 (C^e), 155.9 (C^9), 143.2 (C^4), 134.5 (C^a), 125.4 (C^d) 131.5,(C^c) 128.9 (C^5), 122.2 (C^b), 115.2 (C^f), 113.5, 113.0, (C^6, C^3), 113.1 (C^{10}), 102.0 (C^8), 68.1, 67.2 ($(CH_2)_2$), 52.5, 52.3 (2Me).



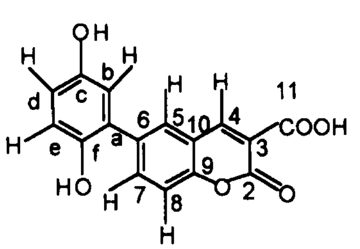
6-amino-3-carbomethoxy coumarin (**10**). A solution of compound **9** (2.3 g, 11.2 mmol) H_2SO_4 (10 ml) in methanol (40 ml) was refluxed for 4 h, cooled and poured into water. The precipitate formed was filtered off, rinsed with water and dried under vacuum. Yield 88%. Mp = 213°C. IR (cm^{-1}), 3430, 3356, 3248 (NH_2), 3065, 3003 (CH arom), 2953, 2849 (CH aliph), 1751, 1705 (C=O), 1645, 1624 (NH_2 bending), 1604, 1577 (C=C arom). ^{1}H-n.m.r. ($CDCl_3$) 8.51 (s, 1H, H^4), 7.13 (d, 1H, $J = 9$ Hz, H^8), 6.99 (d,d, 1H, $J_1 = 9.0$ Hz, $J_2 = 2.7$ Hz, H^7), 6.87 (d, 1H, $J = 2.7$ Hz, H^5), 5.33 (s, 2H, NH_2), 3.80 (s, 3H, CH_3). ^{13}C-n.m.r. 163.4, 156.4 (C^2, C^{11}), 148.8 (C^4),146.3, 145.8 (C^9, C^6), 118.0, 117.1 (C^{10}, C^3), 121.6, 116.4, 111.1 (C^5, C^7 C^8), 52.2 (CH_3).



[6-(3-carbomethoxy)coumarinyl]benzoquinone (**11**). Aminoester **10** (1.16 g, 5.29 mmol) was suspended in AcOH (7 ml) and 16 wt% HCl (15 ml) was quickly added to the mixture at room temperature. A dense white salt formed and was treated with $NaNO_2$ (0.38 g, 5.5 mmol) at 0°C. The clear diazo-solution was added to a solution containing benzoquinone (1.5 g, 13.88 mmol), ethanol (20 ml), water (20 ml) and NaOAc (7 g). The resulting mixture was stirred for 4 h at room temperature. The red precipitate formed was filtered off, rinsed with water, dried under vacuum and chromatogaphed on SiO_2 with chloroform. Yield 58%. Mp = 193°C. IR (cm^{-1}) 3051 (CH arom, olefin), 2955, 2853 (CH aliph), 1768, 1709 (C=O ester) 1655 (C=O quinone), 1614, 1587, 1570, (C=C arom, olefin). ^{1}H-n.m.r. ($CDCl_3$) 8.65 (s, 1H, H^4), 7.92 (d, 1H, $J = 2.3$ Hz, H^5), 7.81 (d,d, 1H, $J_1 = 8.7$ Hz, $J_2 = 2.3$ Hz, H^7), 7.43 (d, 1H, $J = 8.7$ Hz, H^8), 7.00–6.83 (m, 3H, H^b , H^d, H^e), 3.94 (s, 3H CH_3). ^{13}C-n.m.r., 187.0, 186.0 (C^c, C^f), 163.0, 156.1, 155.7 (C^{11}, C^2, C^9), 148.6 (C^4), 143.5 (C^a), 137.0, 136.5 (C^7, C^5), 135.0, 133.0, 130.9 (C^b, C^d, C^e), 134.5 (C^6), 118.4, 117.8 (C^{10}, C^3) 116.8 (C^8), 52.7 (Me).

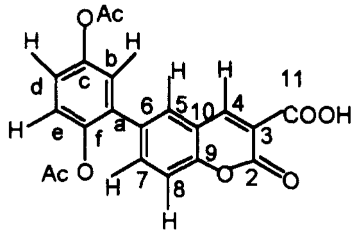


[6-(3-carboxy)coumarinyl]hydroquinone (**12**). Compound **11** (5.0 g, 16.89 mmol), $SnCl_2 \times 2H_2O$ (30 g, 140 mmol) and conc. HCl (300 ml) were stirred for 24 h at 100°C. The precipitate was filtered off, washed with water and dried under vacuum. Yield 70%. Mp = 219°C. IR (cm^{-1}) 3242 (OH), 3040 (CH arom), 1734, 1676 (C=O), 1618, 1574 (C=C arom) ^{1}H-n.m.r. (DMSO-d_6), 8.93 (s, 1H. OH), 8.83 (s, 1H, OH), 8.77 (s, 1H, H^4), 8.00 (d, 1H, $J =$ 1.8 Hz, H^5), 7.87 (d,d, 1H, $J_1 = 1.8$ Hz, $J_2 = 8.4$ Hz, H^7), 7.43 (d, 1H, $J = 8.4$ Hz, H^8), 6.76 (d, 1H, $J = 8.7$ Hz, H^e), 6.70 (d, 1H, $J = 3$ Hz, H^b), 6.62 (d,d, 1H, $J_1 = 8.7$ Hz, $J_2 =$ 3 Hz, H^d). ^{13}C-n.m.r., 163.9, 156.9, 153.1 (C^{11}, C^2, C^9), 150.1, 146.7 (C^c,C^f), 148.4 (C^4), 135.4 (C^6), 135.1, 129.9 (C^5, C^7), 126.2 (C^a), 118.3, 117.6 (C^{10}, C^3), 116.9 (C^8), 116.3, 115.6, 115.4 (C^d, C^e, C^b).



[6-(3-carboxy)coumarinyl]diacetylhydroquinone (**13**). A mixture of compound **12** (0.5 g, 1.67 mmol) and acetic anhydride (10 ml) was refluxed for 4 h. A clear solution formed was poured into water (100 ml) and left overnight to consume excess of acetic anhydride. The precipitate formed was filtered off washed with water dried under vacuum and crystallised from chlorobenzene. Yield 60%. Mp = 151°C. IR (cm^{-1}) 3053 (CH arom), 2950 (CH aliph), 1767, 1738, 1693 (C=O ester), 1622, 1577 (C=C arom).

^{1}H-n.m.r. (DMSO-d_6) 8.79 (s, 1H, H^4), 7.99 (d, 1H, J = 2.1 Hz, H^5), 7.74 (d,d, 1H, J_1 = 2.1 Hz, J_2 = 8.7 Hz, H^7), 7.52 (d, 1H, J = 8.7 Hz, H^8), 7.32 (d, 1H, J = 8.7 Hz, H^e), 7.31 (d, 1H, J = 3.0 Hz, H^b), 7.24 (d,d, 1H, J_1 = 3.0 Hz, J_2 = 8.7 Hz. H^d), 2.30 (s, 3H. CH_3), 2.12 (s, 3H, CH_3). ^{13}C-n.m.r., 169.1, 168.9 ($2OCOCH_3$), 163.8, 156.5, 153.9 (C^{11}, C^2, C^9), 148.2, 144.8 (C^c,C^f), 148.0 (C^4), 134.1, 129.8 (C^5, C^7), 133.2, (C^6), 132.5 (C^a), 124.2, 123.4, 122.4 (C^d, C^e, C^b), 118.9, 118.1 (C^3, C^{10}) 116.4 (C^8), 20.7, 20.5 ($2CH_3$).



Polymerization

Poly-6-2 and **Poly-6-10**. Monomer **6** (0.500 g, 1.255 mmol) and ethylene glycol (0.16 g, 0.258 mmol) or 1,10-decanediol (0.218 g, 1.252 mmol) were heated at 200°C for 1 h under nitrogen flow. Then the pressure was reduced to 0.1 mm Hg and the reaction was heated for 1 h more at 250°C. The polymers were precipitated from chloroform into methanol and dried under vacuum until constant weight.

Poly-13, **Poly-13-25**, **Poly-13-50** and **Poly-13-75**. Monomer **13** (0.2–0.3 g) or its mixture with *m*-acetoxybenzoic acid were heated at 200°C for 1 h under nitrogen flow. Then the pressure was reduced to 0.1 mm Hg and the reaction was continued for 1 h more at 330°C. The polymers were dissolved in chloroform, precipitated into methanol and dried under vacuum until constant weight.

Measurements and sample preparation

The number average molecular weights of polymers was determined by ^{1}H-n.m.r. analysis of the end groups and by GPC (a Varian 9012 GPC instrument at 30°C in $CHCl_3$ with polystyrene standard, universal column and a flow of 1 ml/min). DSC, TMA and TGA were performed at a heating rate of 10°C/min under nitrogen with a du Pont 2100 machine. Glass transition (T_g) and softening temperatures (T_s) were determined from DSC and TMA curves, respectively. FT-IR-spectra were taken using a Nicolet 510p spectrometer. UV-visible spectra were taken using a Shimadzu UV-260 spectrometer in thin films spin-coated onto a quartz slide. ^{1}H-n.m.r. and ^{13}C-n.m.r. spectra were taken using a Varian spectrometer at 300 MHz and 75.5 MHz, respectively, in DMSO-d_6 or $CDCl_3$ with TMS as the internal standard. Emission and excitation spectra were measured with a Perkin-Elmer 630-10S fluorimeter using thin films spin-coated onto a quartz slide.

Determination of the degree of branching

The degree of branching (*DB*) of **Poly-13** and hyperbranched copolymers, which represents the number of branches per repeating unit, was calculated from ^{1}H-n.m.r. signals of terminal Ac groups.

For **Poly-13** *DB* is:

$$DB = I_1/I_2, \tag{1}$$

where I_1 and I_2 are the integrals of Ac and Ac′ in the case of **Poly-13** (*Figure 2*).

In the case of hyperbranched copolymers **Poly-13-25**, **Poly-13-50** and **Poly-13-75** *DB*s were calculated according to the following formula:

$$DB = \frac{I_1}{(I_2 + I_3)M}, \tag{2}$$

where I_1, I_2 and I_3 are the integrals of Ac_1, Ac_2 and Ac_3, respectively (*Figure 3*) and M is the molar ratio of monomer **13** in copolymer (determined from ^{1}H-n.m.r. spectra).

RESULTS AND DISCUSSION

Monomer and polymer synthesis

The synthetic route to monomer **6** included the alkylation of 7-hydroxycoumarin (**4**) with excess of 1,2-dichroroethane to give 7-(2-chloroethoxy)coumarin (**5**) which then produced monomer **6** on treating with previously synthesized dimethylhydroxyterephthalate (**3**) (*Scheme 1*).

The key step in the synthesis of monomer is the Meerwein reaction between benzoquinone and diazonium salt of 6-amino-3-carbomethoxy coumarin (**10**) giving intermediate **11** (*Scheme 1*). The diazonium salt was generated from coumarin-3-carboxylic acid by the nitration followed by the reduction of the nitro group and the esterification of the 3-carboxy group. The resulting aminoester **10** was diazotated to give a diazonium salt. Quinone **11** was reduced to hydroquinone **12** by $SnCl_2$ in conc. HCl under reflux with simultaneous hydrolysis of 3-carbomethoxy group. Monomer **13** was prepared from hydroquinone **12** by the acylation of phenolic hydroxy-groups with acetic anhydride.

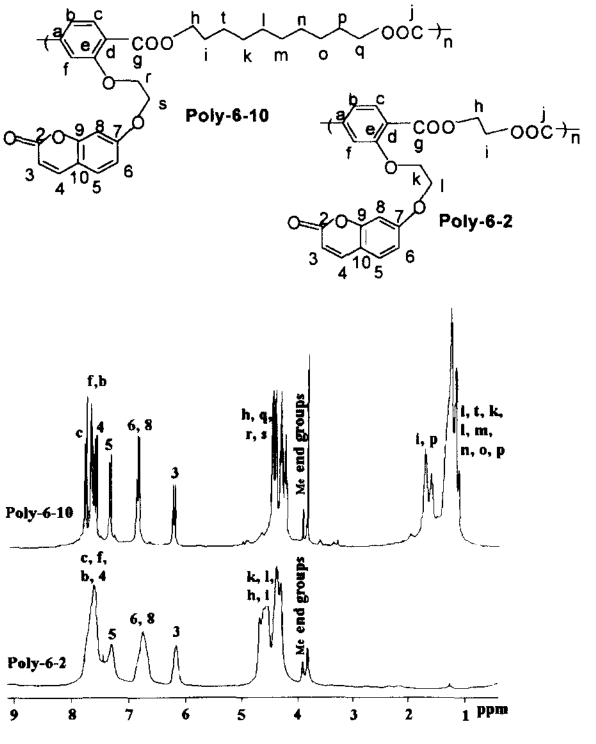
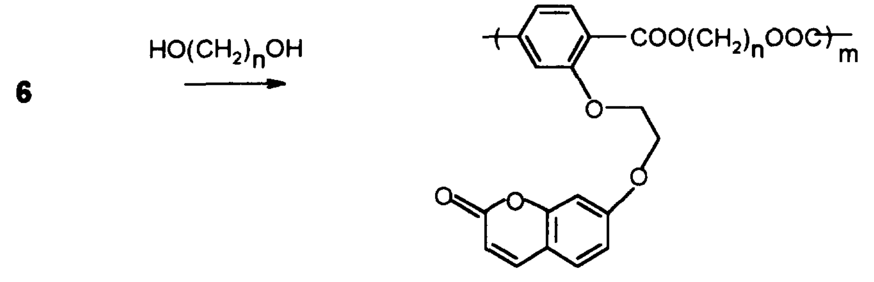
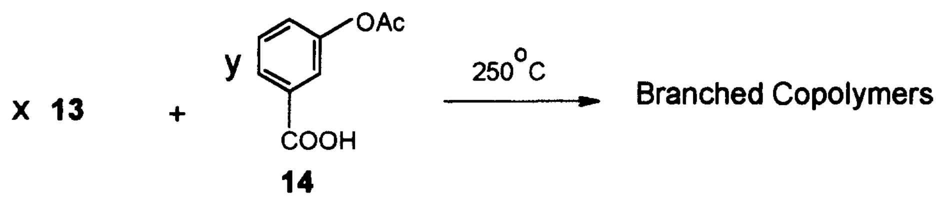


Figure 1 ^{1}H-NMR spectra of polymers **Poly-6-2** and **Poly-6-10**



n = 2 **Poly-6-2**

n = 10 **Poly-6-10**



Copolymer	X (molar ratio)	Y (molar ratio)
Poly-13-25	0.25	0.75
Poly-13-50	0.50	0.50
Poly-13-75	0.75	0.25

An alternative route to **13** from **11** was investigated. It included the reduction of quinone **11** under mild conditions without hydrolysis of 3-carbomethoxy group followed by the alkaline hydrolysis of the resulting [6-(3-carbomethoxy)coumarinyl]hydroquinone to give compound **12**. However, the hydrolysis of 3-carbomethoxy group under basic conditions cleaved pyrone ring, probably, by the Michael addition of hydroxy anion to the double bond followed by the rupture of C^3—C^4 link[17]. Therefore, the acid hydrolysis was the only one acceptable in this case.

All polymers were prepared by the high-temperature transesterification in melt (*Scheme 2*). It was shown earlier[14] that pyrone ring of coumarin was stable at high temperature polycondensation conditions and no cross-linking ring took place due to the cleavage of pyrone. *Figure 1* shows ^{1}H-n.m.r. spectra of polymers **Poly-6-2** and **Poly-6-10**. The assignment of signals corresponds to the proposed structure. Both spectra show a series of signals in the region of 7.40–7.20, 7.00–6.60 and 6.30–6.00 ppm (H^5, H^6, H^8 and H^3) with correct proton ratio belonging to coumarin protons. The more resolved spectrum of **Poly-6-10** allows us to identify H^4 as a doublet at 7.65 with $J = 9.3$ Hz, the aliphatic protons appeared in the region 4.80–1.00 ppm. The number average molecular weight (M_n) was rather low for both polymers corresponding to the degree of polymerization of 7–8 (*Table 1*), GPC data also confirmed low molecular weight of the polymers. The reason for the low molecular weight can be found by the examination of the ^{1}H-n.m.r. spectra of the polymers. Both polymers showed signals of terminal carbomethoxy groups (two singlets at 3.94–3.91 and 3.86–3.82 ppm). The first signal corresponds to methyl of C^j (*metha* to phenolic oxygen) and the second to methyl of C^g (*ortho* to phenolic oxygen). As can be seen from the *Figure 1* the integral of the first signal is less than that of the second by a factor of 4–5. This means that two carbonyls of terephthalic moiety of monomer **6** have different reactivity with respect to transesterification and the first (C^j) is more reactive than the second (C^g). The difference in the reactivity can be explained by the joint action of steric and electronic factors; the bulky coumarin group in the *ortho* position together with the electron donating effect of phenolic oxygen make C^g carbonyl less sensitive to the nucleophylic attack of diol hydroxyl. When polycondensation started the more reactive C^g carbonyls reacted first forming oligomers with terminal C^J carbonyls which undergo the transesterification only slowly.

Hyperbranched polymer **Poly-13** was prepared similarly to **Poly-6-2** and **Poly-6-10** by the high temperature transesterification in melt but at higher temperature (330°C). **Poly-13** is completely soluble in chloroform providing support that no cross-linking occurred during the polycondensation.*Figure 2* presents ^{1}H-n.m.r. and ^{13}C-n.m.r. spectra of **Poly-13.** The signal assignment corresponds to the proposed dendrimeric structure. ^{1}H-n.m.r. spectra prove the perfect dendrimeric structure of the polymer. Thus, the ratio of Ac to Ac′ end group signals (2.25 and 2.05 ppm, respectively) of **Poly-13** and that of H^4 to $H^{4'}$ protons (8.80 and 8.60 ppm, respectively) belonging to the inner and outer layer of coumarin moieties of dendrimer equal to 1 within the limits of experimental error of n.m.r. analysis (5–10%), suggest the polymer is a dendrimer with $DB = 1$. The availability of only two peaks in the region of 8.80–8.60 ppm shows that **Poly-13** has few, if any, defects of branching. The ^{13}C-n.m.r. spectra provide further confirmation for polymer structure; OAc and OAc′ end groups appeared at 169.1, 21.0 and 169.0, 20.8 ppm (C=O and CH_3, respectively,). C^4 (inner layers) and $C^{4'}$ (outer layer) appeared as a doublet at 150.6, and 148.5 ppm. The number average molecular weight (M_n) of **Poly-13** was calculated from ^{1}H-n.m.r. spectra by the end group analysis. **Poly-13** gave M_n of 27 000 corresponding to the degree of polymerization (*DP*) of 60 which is in reasonable agreement with the data of GPC (*Table 1*). Unlike linear polymers, the number of end groups per repeating unit for hyperbranched polymers derived from monomers of AB_2 type approaches 1, not 0, with molecular weight.

Various copolymers have been prepared by the copolycondensation of monomer **13** with *m*-acetoxybenzoic acid to relate the polymer properties with the density of branching. *Figure 3* shows ^{1}H-n.m.r. spectra of copolymers. As can be seen the ratio of the signal at 8.80 to 8.60 ppm increases with molar ratio of *m*-acetoxybenzoic acid. These peaks belong to coumarin H^4 protons of the inner and outer layers, respectively. *DB* of copolymers was calculated from n.m.r. spectra (see Experimental); the signal at 2.30 ppm is assigned to methyls of Ac^1 and Ac^3, while the peak at 2.05 ppm is due to the methyl of Ac^2 end groups. The ratio of the two peaks is equal to that of coumarin H^4 protons for the respective copolymers, which also confirmed the perfect branching for all three copolymers. Similar to **Poly-13**, *DB*s of the copolymers were found to be equal to 1 within the limits of experimental error of n.m.r. analysis (5–10%). As in the case of homopolymer **Poly-13**, the molecular weight of copolymers was determined by the end group n.m.r. analysis and GPC, taking into account that in the case of random copolymerization of monomers AB_2 and AB type the number of B groups per unit approaches the molar ratio of AB_2 monomer with molecular weight. The data are listed in *Table 1*

The high *DB*s of the synthesized hyperbranched polymers might be due to the high temperatures of the polymerization. Under these conditions the high mobility of the polymer chains diminishes steric hindrances thus promoting the complete reaction between functional groups.

Polymer properties

As can be seen from *Table 1* all polymers derived from monomer **13** show medium molecular weight while polymers produced from monomer **6** gave only oligomers. All polymers were completely soluble in chlorinated organic solvents like chloroform and dichloromethane giving transparent films with good quality when cast from chloroform. Only **Poly-6-10** gave opaque films due to the crystallinity of the polymer. All polymers excepting **Poly-6-10** were amorphous which followed from their DSC curves; no endotherms were observed in their DSC traces. **Poly-6-10** exhibited an endotheric peak with a maximum at around 90°C assigned to the melting transition taking into account T_s of the polymer. The crystallinity of **Poly-6-10** is related to the decamethylene spacer and low molecular weight making it easy for the polymer chain to be packed. T_g and T_s of hyperbranched polymers derived from monomer **13** tend to increase with the monomer **13** ratio, while the thermostability decreases in the same direction. The increase of T_g and T_s is related to the fact that monomer **13** is more rigid than **14**. On the other hand, as already noted in the case of random copolymerization of monomers AB_2 and AB type, the ratio of B groups to the monomer unit approaches the molar ratio of AB_2 monomer with the molecular weight and hence increases with the monomer **13** portion in copolymers. This phenomenon contributes to the decrease in the thermostability of hyperbranched copolymers with the increase in monomer **13** content (*Table 1*).

Figure 4 represents absorption spectra of **Poly-6-2**, **Poly-6-10** and **Poly-13**. The long wave absorption maxima at

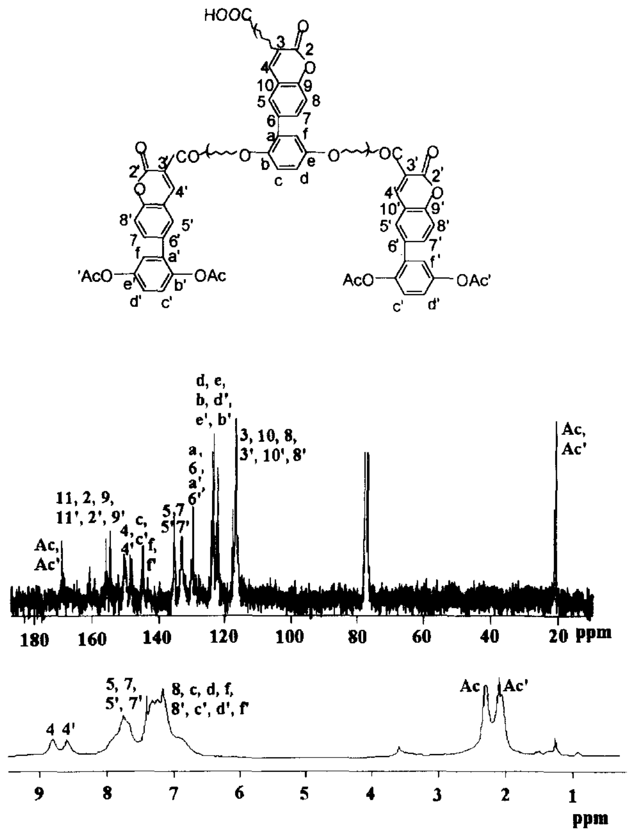


Figure 2 ^{1}H-NMR and ^{13}C-NMR spectra of **Poly-13**

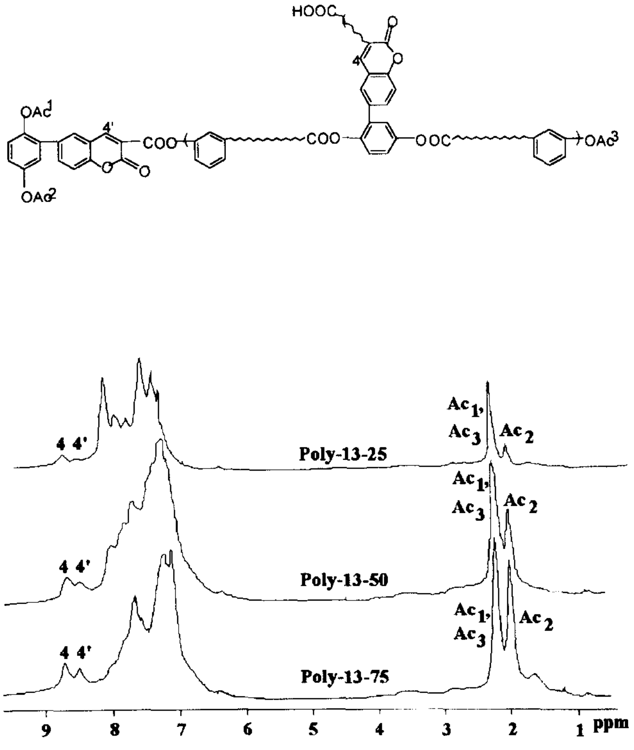
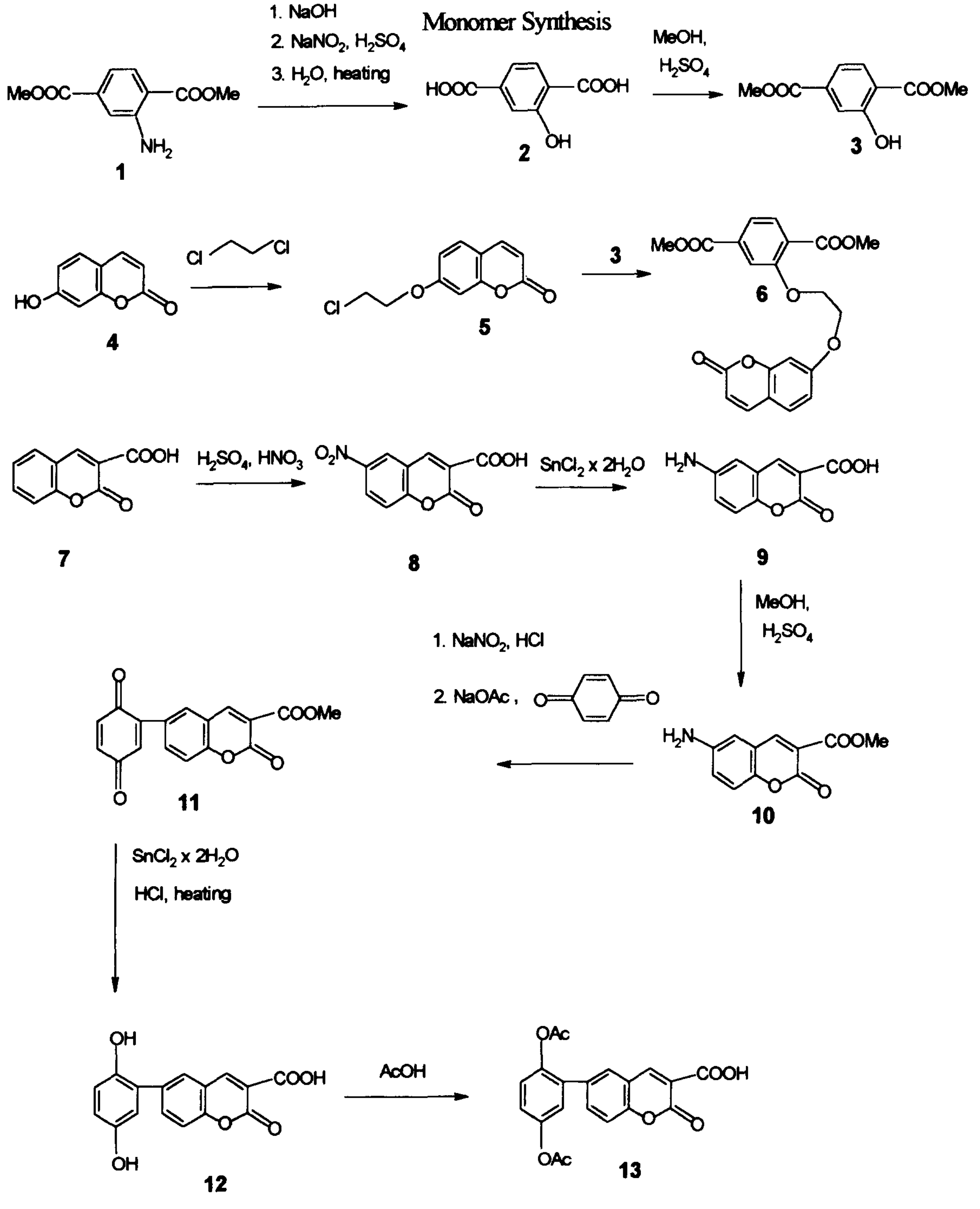


Figure 3 ^{1}H-NMR spectra of copolymers **P-13-75**, **P-13-50** and **P-13-75**

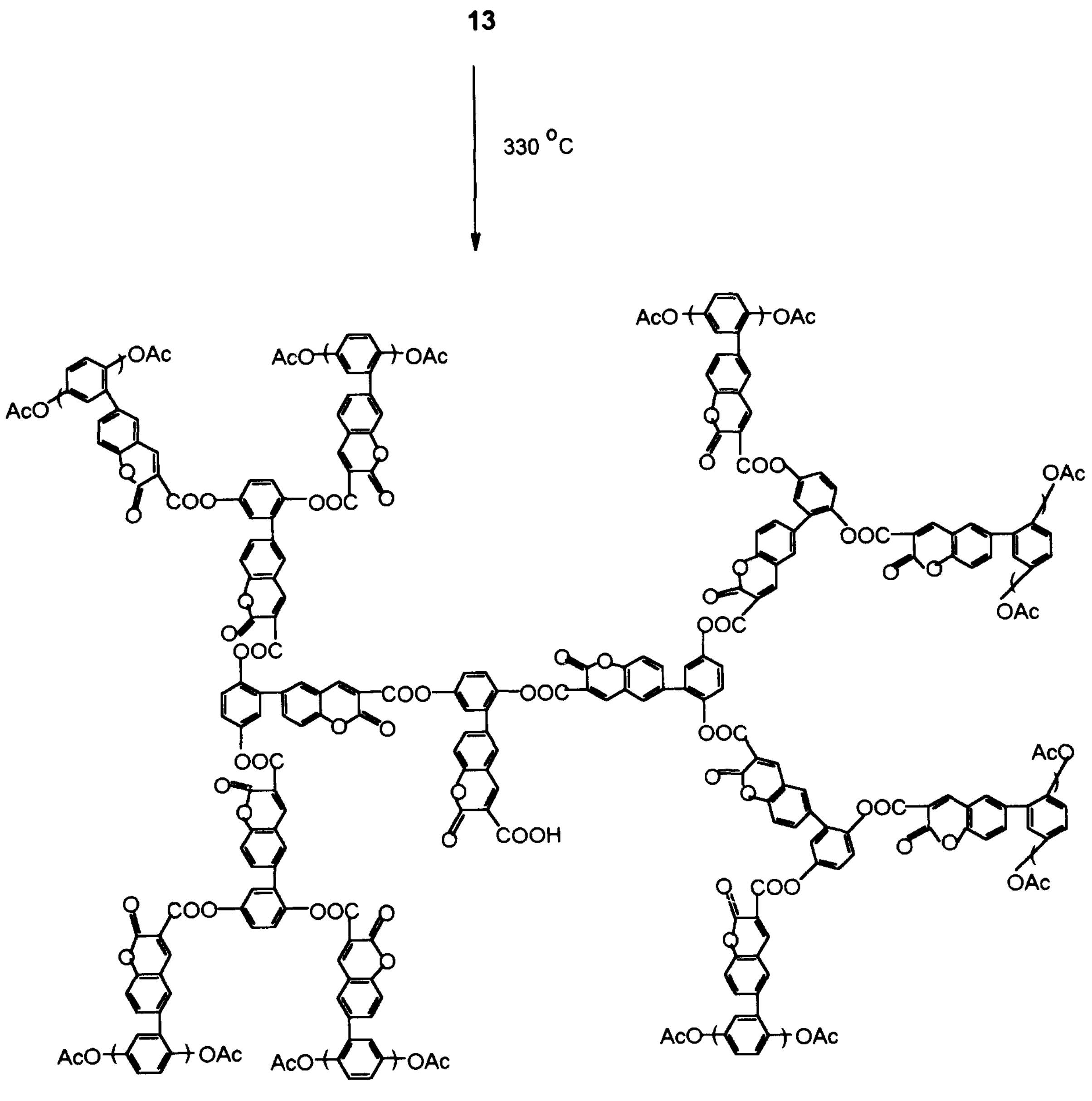
around 320 and 350 nm are due to the 7-alkoxycoumarin and 6-phenylcoumarin chromophore of **Poly-6-2**, **Poly-6-10** and **Poly-13**, respectively. The spectra of copolymers **Poly-13-25**, **Poly-13-50** and **Poly-13-75** are similar to those of **Poly-13** with less intensive long wave absorption maxima. All polymers showed strong photoemission in solution and film due to the coumarin moiety. Both emission and excitation spectra showed a broad structureless peak with the maxima listed in *Table 1*. As seen, the polymers are blue emitters emitting in the range of 450–490 nm when excited at 400 nm. No appreciable shift of emission maxima was observed for hyperbranched copolymers under the change of monomer **13** ratio, suggesting no interaction between chromophores which is probably concerned with steric hindrance in hyperbranched polymers.

Single layer EL devices with **Poly-6-2**, **Poly-13**, **Poly-13-75** and **Poly-13-50** have been made. The device consists of ITO coated glass, polymer (dissolved in chloroform and spin-cast for thickness of 100–200 nm), Mg—Al (9:1) alloy cathode with 200 nm of thickness was deposited directly on the top of the polymer film under vacuum. *Figure 5* presents current density–voltage relationships for the fabricated devices. As can be seen the higher the concentration of coumarin units in polymer the lower turn on voltage. The electroluminescence spectra of the polymers were similar to their photoluminescence spectra.



Scheme 1

Polymer Synthesis



Scheme 2

Table 1 Some physico-chemical properties of synthesised polymers

Polymer	Yield(%)	M_n(× 10^3)	DP	T_g(°C)	T_m^a(°C)	T_{10}^b(°C)	T_s(°C)	λ_{em}^c(nm)	λ_{ex}^d(nm)	λ_{max}^e(nm)	M_n^f(× 10^3)	PD^g
Poly-6-2	78	2.8	7	100	—	400	135	451	394	319	2.1	1.4
Poly-6-10	81	4.0	8	—	90	390	80	450	371	317	4.5	1.5
Poly-13	95	27	60	230	—	370	315	484	439	351	28	2.5
Poly-13-25	96	43	250*	160	—	415	220	497	449	346	37	2.6
Poly-13-50	94	28	120*	190	—	400	290	484	435	352	21	2.3
Poly-13-75	97	46	170*	215	—	400	310	492	444	347	54	2.7

[a] Melting point
[b] 10% weight loss temperature
[c] Emission maximum, excitation at 400 nm
[d] Excitation maximum, emission at 480 nm
[e] Long wave absorption maximum
[f] M_n determined by GPC
[g] Polydispersity determined by GPC
[*] The sum of AB_2 and AB monomer unit over one macromolecule

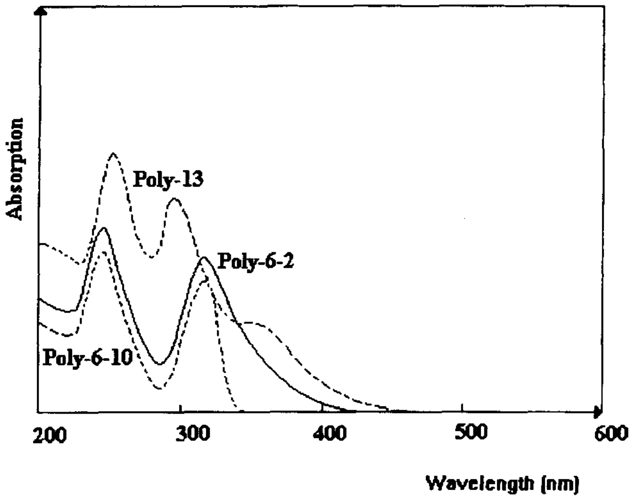


Figure 4 Absorption spectra of **Poly-13**, **Poly-6-2** and **Poly-6-10**

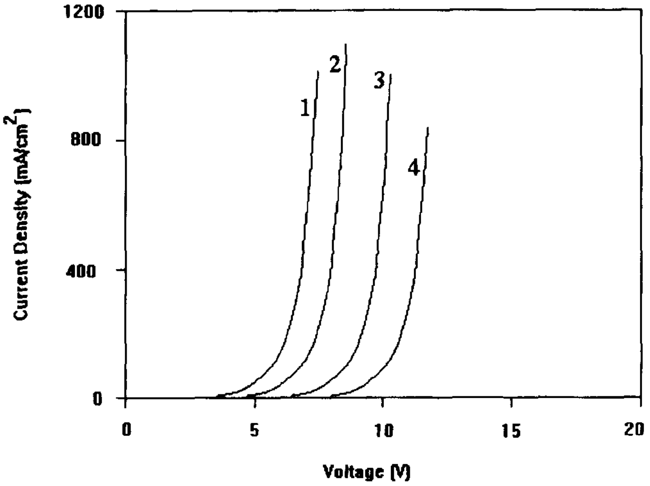


Figure 5 Current density–voltage relationship for EL devices; **Poly-13** (**1**), **Poly-13-75** (**2**), **Poly-6-2** (**3**) and **Poly-13-50** (**4**)

CONCLUSIONS

Novel coumarin-containing monomers [6-(3-carboxy)coumarinyl]diacetylhydroquinone (**13**) and [2-(7-cumarinyloxy)ethoxy]dimethyl terephthalate (**6**) have been synthesized and polymerized to give hyperbranched and comb-like coumarin-containing polyesters. The polymers showed low to medium molecular weights and were soluble in chlorinated aliphatic solvents to give film with good optical quality when cast. All polymers excepting one were amorphous with T_g in the range of 100–230°C and thermostability of 370–415°C. All hyperbranched polymers exhibited *DB* close to 1. The polymers were found to be blue emitters emitting light in the range of 450–492 nm.

ACKNOWLEDGEMENTS

This work was supported by a Grant from CONACyT with contract N 0087-PN. Thanks are also due to M. A. Canseco, R. Gaviño, and C. Vazquez for their assistance in UV spectroscopy, n.m.r.-analysis and thermal analysis, respectively.

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