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# Copolymers derived from 7-acryloyloxy-4-methylcoumarin and acrylates: 1. Copolymerizability and photocrosslinking behaviours

**Yun Chen* and Juin-Lyang Geh**
*Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan 701, Republic of China*
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Photoreactive copolymers containing 4-methylcoumarin pendant groups were prepared by radical copolymerization of 7-acryloyloxy-4-methylcoumarin ($M_1$) with acrylates [$M_2$ = methyl methacrylate (MMA), methyl acrylate (MA), ethyl acrylate (EA) and butyl acrylate (BA)] in dimethyl formamide (DMF) at 65°C using azobisisobutyronitrile as initiator. The monomer reactivity ratios (MRRs) of $M_1$ and $M_2$ were estimated by the Fineman–Ross and Kelen–Tüdos methods, by analysing copolymer compositions which were determined by $^1$H nuclear magnetic resonance (n.m.r.) spectra. It was found that the MRRs are $r_1 = 0.45$, $r_2 = 1.68$ for $M_1$–MMA; $r_1 = 2.16$, $r_2 = 0.48$ for $M_1$–MA; $r_1 = 2.04$, $r_2 = 0.42$ for $M_1$–EA; $r_1 = 1.82$, $r_2 = 0.53$ for $M_1$–BA, respectively. The order of monomer reactivity estimated from $1/r_1$ values is MMA > $M_1$ > BA > EA > MA. The higher reactivity of MMA can be attributed to its extra hyperconjugating stabilization by methyl groups in addition to C=O conjugation. Furthermore, from $^{13}$C n.m.r. spectra, it was found that $\pi$-electron density of the $\beta$-carbon is in the order of MA > EA > BA > $M_1$. The lower electron density of $\beta$-carbons in a monomer leads to easier electron transfer from propagating radical to the monomer and consequently a higher reactivity. Photocrosslinking (300 nm) of the copolymers in the film state were investigated by their characteristic curves ($W/W_0$ *versus* time plot). Copyright © 1996 Elsevier Science Ltd.

**(Keywords: 7-acryloyloxy-4-methylcoumarin; acrylates; copolymerization)**

## INTRODUCTION

Photosensitive polymers are often used in the fields of printing, ink[1,2], and coating[3]. Especially in electronics, the development of photosensitive polymers makes the technology of integrated circuits (ICs), large scale integrated circuits (LSIs), very large scale integrated circuit (VLSIs) so important that causes the revolution of the calculators and many electronic machines. As a result, many laboratories still keep on exploring the field of the photosensitive polymers.

At present, it is defined that photosensitive polymers are those with photosensitive groups in the main or pedant chains, which crosslink or cleave after irradiation with u.v. light (or electron beam) depending on whether it is negative- or positive-type[3]. In general, for negative-type there are three kinds of photosensitive groups used widely, i.e. azide groups[4], cinnamate groups[5], and diazo groups[6]. And their solubility in the developer is greater for light-unexposed than exposed areas, leading to formation of patterns by removal of unexposed zones. Four-centre type photopolymerization and [2 + 2] photopolymerization in solid state have been studied in detail by Hasegawa[7–9]. Right now many researchers are still trying to synthesize new and useful photosensitive polymers and investigate their potential applications.

Coumarin, 2-chromenone, exists in trace amounts in many plants particularly in some kind of fruits, as a component in aromatic flavours[10]. In 1902, Ciamician and Silber found that coumarin dimerized on photoirradiation ($\lambda_{max} > 300$ nm) in ethanol or in an aqueous medium[11]. Since then, the photocyclodimerization of coumarin have received a lot of attention among organic chemists and has been studied extensively by several groups both from the synthetic and mechanistic points of view[12–18]. Coumarin yields four types of dimers on photoirradiation, of which the product ratio is influenced predominantly by the multiplicity in the [2 + 2] photochemical reactions. The structures of these dimers are *anti* head-to-head, *anti* head-to-tail, *syn* head-to-head, and *syn* head-to-tail types. Moreover, Krauch and coworkers reported the cycloreversion (photocleavage) of *anti* head-to-head coumarin dimer in dioxane into the starting coumarin upon photoirradiation with wavelengths shorter than 300 nm[14].

Similarly, *o*-acetylumbelliferone derived from umbelliferone (7-hydroxycoumarin) readily photodimerizes to form *anti* head-to-head *o*-acetylumbelliferone dimer in a dichloromethane solution[19]. Dicoumarins have also been synthesized from condensation of diacid chlorides with umbelliferone or 4-methylumbelliferone and their

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* To whom correspondence should be addressed

photopolymerization behaviour under 350 nm has been studied in detail[20,21]. Moreover, 7-acryloyloxy-4-methylcoumarin has also been prepared from umbelliferone and copolymerized with *N*-(1-phenylethyl)acrylamide[22]. Under photoirradiation with u.v. light having $\lambda_{max}$ = 350 nm, the copolymer crosslinks readily by cyclodimerization of pendant coumarin chromophores. However, the coumarin dimer chromophores cycloreverse to original coumarin chromophores under 254 nm light. This indicates that the photoreaction reversibility of coumarin chromophores is not influenced by its substitution at 7-position.

In this work, photosensitive copolymers were prepared from 7-acryloyloxy-4-methylcoumarin ($M_1$) and acrylates [$M_2$ = methyl methacrylate (MMA), methyl acrylate (MA), ethyl acrylate (EA) and butyl acrylate (BA)] by radical copolymerization using asobisisobutyronitrile (AIBN) as radical initiator. The monomer reactivity ratios were estimated by Fineman–Ross and Kelen–Tüdos methods. Relative reactivity of these monomers has been discussed in detail. Glass transition temperatures ($T_g$s) of the copolymers were determined by differential scanning calorimetry (d.s.c.). Photocrosslinking behaviours in the film state were investigated by establishing their characteristic curves.

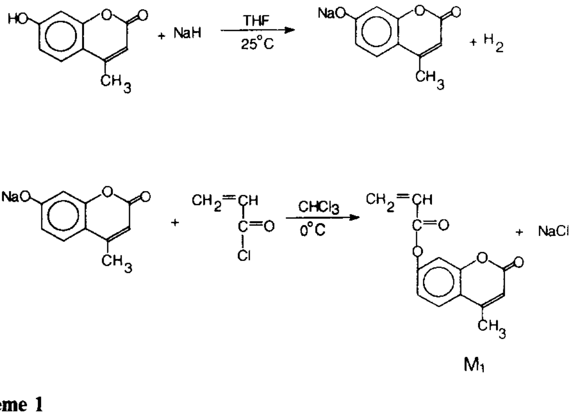
## EXPERIMENTAL

### *Chemicals*

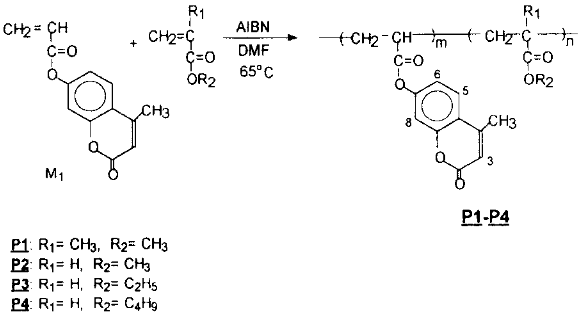
Acryloyl chloride and 7-hydroxy-4-methylcoumarin were purchased from Merck and Tokyo Chemical Co., respectively, and used without further purification. MMA, MA, EA and BA were all purchased from Wako Chemical Co. and purified by vacuum distillation. AIBN was from Wako Chemical Co. and used as received. *N*, *N*-Dimethylformamide (DMF) was purified by vacuum distillation after drying with barium oxide. Other solvents and chemicals were pure reagents and used as received or purified by the conventional methods.

### *Synthesis of 7-acryloyloxy-4-methylcoumarin ($M_1$)* (Scheme 1)

7-Hydroxy-4-methylcoumarin (20 g, 113 mmol) and sodium hydride (6 g, 150 mmol; 60% dispersed in oil) were added to tetrahydrofuran (600 ml). The mixture was allowed to react for 3 h at ambient temperature. After complete evaporation of the solvent, the solids were dispersed in chloroform (600 ml) and cooled to 0°C. Under vigorous stirring, acryloyl chloride (11 g, 120 mmol) was injected into the mixture by a syringe and the reaction was continued for 1 h. The white solids, obtained by evaporating chloroform, were recrystallized in acetone. Yield 75%; mp = 155–157°C; infra-red (i.r.) (KBr) $\nu$ 1770–1750 (–COO–); 1737 cm$^{-1}$ (lactone). $^1$H nuclear magnetic resonance (n.m.r.) (DMSO-$d_6$) $\delta$ 2.43 (*s*, 3H, $\mathrm{C\underline{H}_3}$); 6.07 [*d*, 1H, *trans* $-\mathrm{C\underline{H}_2{=}CH}-$]; 6.25 [*s*, 1H, $\phi-\mathrm{C(CH_3){=}C\underline{H}{-}COO}-$]; 6.65 (*d*, 1H, *cis* $\mathrm{C\underline{H}_2{=}CH}-$); 6.3, 6.34, and 6.39 (*t*, 1H, $\mathrm{CH_2{=}C\underline{H}{-}COO}-$); 7.09–7.64 ppm (*m*, 3H, aromatic protons). Anal. Calcd for $C_{13}H_{10}O_4$: C, 67.85%; H, 4.35%. Found: C, 67.81%; H, 4.37%.



**Scheme 1**



**Scheme 2**

### *Copolymerization of $M_1$ with acrylates* (Scheme 2)

Copolymerization of 7-acryloyloxy-4-methylcoumarin ($M_1$) with the acrylates was conducted in DMF at 65°C using AIBN as initiator. For example, into a 50-ml two-necked glass reactor were added 7-acryloyloxy-4-methylcoumarin (2.0 g, 8.7 mmol), MMA (1.74 g, 17.4 mmol), and DMF (20 ml). The mixture was purged with dry nitrogen and heated slowly to 65°C under gentle stirring. A solution of AIBN (2 wt% monomers) in DMF was injected by a syringe to the mixture under vigorous stirring. The mixture was allowed to react for 6 h under nitrogen blanket. The copolymer P1 was isolated by reprecipitation in a large amount of ethanol. Yield 85%, reduced viscosity $\eta_{red}$ = 0.21 dl g$^{-1}$ ($c$ = 0.3 g dl$^{-1}$ CHCl$_3$, 30°C). I.r. (KBr) $\nu$ 1733 (lactone); 1758 (ester); 1615 cm$^{-1}$ (C=C of lactone). $^1$H n.m.r. (CDCl$_3$) $\delta$ 3.4–3.8 (*br*, $-\mathrm{COO{-}C\underline{H}_3}-$); 6.25 [*br*, $-\phi-\mathrm{C(CH_3){=}C\underline{H}}-$ CO–]; 7.0–7.7 ppm (*br*, $\mathrm{C_6\underline{H}_3}-$).

The copolymers used for elemental analysis were prepared by similar procedures. However, the monomer compositions (mol%) were varied as shown in Tables 1–4 and the conversions were limited to lower than 5% by controlling polymerization time. This polymerization time was estimated to be about 5 min from conversion *versus* time plots of several separate experiments.

### *Measurements*

I.r. spectra of the monomers and copolymers were recorded using an i.r. spectrophotometer, model IR-810 from Japan Spectroscopic Co., at a resolution of 4 cm$^{-1}$. Melting points were determined on a Fargo MP-1D and are uncorrected. $^1$H n.m.r. and $^{13}$C n.m.r. spectra were recorded using a Bruker 200 MHz spectrometer with tetramethylsilane as internal standard. The reduced viscosity of copolymers was measured at 30°C using an Ostwald viscometer, the concentration was about 0.3 g dl$^{-1}$ in chloroform. Differential scanning

**Table 1** Copolymerization of $M_1$ and acrylates $M_2$[a]

| Comonomer | Feed $[M_1]/[M_2]$ | Conversion (%) | $\eta_{red}$ (dl $g^{-1}$)[b] | Copolymer composition (%)[c] | |
|---|---|---|---|---|---|
| | | | | $M_1$ | $M_2$ |
| $M_1$ | 1/0 | 73 | 0.11 | 100 | |
| $M_1$–MMA | 1/2 | 85 | 0.21 | 31.5 | 68.5 |
| $M_1$–MA | 1/2 | 77 | 0.23 | 38.1 | 61.9 |
| $M_1$–EA | 1/2 | 75 | 0.22 | 36.5 | 63.5 |
| $M_1$–BA | 1/5 | 82 | 0.26 | 23.9 | 76.1 |

[a] Copolymerized in DMF at 65°C for 6 h using AIBN as initiator
[b] Measured at 0.3 g $dl^{-1}$ chloroform at 30°C
[c] Estimated from $^1H$ n.m.r. spectra of copolymers

**Table 2** Copolymerization of $M_1$ with MMA[a]

| Monomer composition (mol%) | | Copolymer yield (%) | Viscosity[b] $\eta_{red}$ (dl $g^{-1}$) | Copolymer[c] composition (mol%) | |
|---|---|---|---|---|---|
| $M_1$ | MMA | | | $M_1$ | MMA |
| 24.87 | 75.13 | 3.9 | 0.20 | 15.6 | 84.4 |
| 33.29 | 66.71 | 3.7 | 0.26 | 21.9 | 78.1 |
| 38.27 | 61.73 | 4.6 | 0.18 | 26.6 | 73.4 |
| 40.3 | 59.3 | 2.2 | – | 26.3 | 73.7 |
| 50 | 50 | 4.8 | 0.24 | 34.9 | 65.2 |
| 71.1 | 28.9 | 5.0 | 0.23 | 56.9 | 43.1 |
| 74.62 | 25.38 | 4.9 | 0.19 | 58.3 | 41.7 |

[a] Copolymerized in DMF at 65°C using AIBN as initiator
[b] Measured at 0.30 g $dl^{-1}$ chloroform at 30°C
[c] The compositions were calculated from the peak areas of $^1H$ n.m.r. spectra

calorimetric (d.s.c.) thermograms of the copolyacrylates over the temperature range of −70 to 200°C were recorded using a DuPont 910 thermal analyser at a heating rate of 20°C $min^{-1}$ and a sensitivity of 5 mcal $s^{-1}$ under nitrogen purging.

### *Photocrosslinking experiments*

A Rayonet photochemical reactor, model RPR-100, was used in all photocrosslinking experiments. The photochemical reactor was equipped with 16 tubes of 300 nm lamps for photocrosslinking of the copolymers in the film state. The film samples used in the irradiation experiment were prepared by casting the copolymer solution (ca. 0.01 g per 5 ml chloroform) on the outside surface of a quartz cell followed by evaporation of the solvent. The thickness of the dried film was about 100–150 $\mu$m. They were then put in the centre of the photochemical reactor for irradiation experiment. When sixteen lamps were used, the energy was about 400 W and the temperature inside the reaction chamber was about 36°C.

## RESULTS AND DISCUSSION

### *Copolymerization of 7-acryloyloxy-4-methylcoumarin ($M_1$) and acrylates ($M_2$)*

We have previously reported the synthesis and photoreaction kinetics of photoreactive copolymer derived from 7-acryloyloxy-4-methylcoumarin ($M_1$) and *N*-(1-phenylethyl)acrylamide ($M_2$)[22]. Their monomer reactivity ratios are $r_1 = 1.22$, $r_2 = 0.11$, and $r_1 = 1.28$, $r_2 = 0.16$ as estimated by the Fineman–Ross and Kelen–Tüdos methods, respectively. Poly(ethyleneimine) with coumarinyl pendant groups has been prepared by Chuo *et al.* and its photocrosslinking properties investigated by u.v. spectral change[23]. In this work, 7-acryloyloxy-4-methylcoumarin ($M_1$) is first copolymerized with four acrylate monomers (MMA, MA, EA, and BA) to prepare photoreactive copolyacrylates with 4-methylcoumarin pendant chromophores.

As shown in *Table 1*, 7-acryloyloxy-4-methylcoumarin ($M_1$) readily copolymerizes with these acrylate monomers. The copolymer yields are greater than 75% and their reduced viscosities ($\eta_{red}$) are in the range of 0.21–0.26 dl $g^{-1}$. Furthermore, mol% of 7-acryloyloxy-4-methylcoumarin ($M_1$) in the copolymers P2–P4 are greater than those in the feed, indicating that $M_1$ is more easily incorporated into the copolymers than MA, EA, and BA. On the contrary, for copolymer P1, the mol% of $M_1$ is less than that in the feed, indicating that the reactivity of MMA is greater than $M_1$. These qualitative results could not be used to predict copolymer composition of other feed systems since they are the cumulative composition of the resultant copolymers. Therefore, it is important to estimate the monomer reactivity ratios (MRRs) of each comonomer pair to predict copolymer composition. Relative reactivity of these comonomers are also interesting from both academic and practical point of view and can be derived from the monomer reactivity ratio $1/r_1$ ($= k_{12}/k_{11}$).

### *Copolymerizability of $M_1$ and $M_2$*

To investigate the copolymerization behaviours of 7-acryloyloxy-4-methylcoumarin ($M_1$) with acrylates ($M_2$), their MRRs ($r_1$ and $r_2$) were first calculated from feed and copolymer compositions by two different methods using $^1H$ n.m.r. spectral data. In $^1H$ n.m.r. spectra of the copolymers, the chemical shift of the four protons in coumarin chromophore (*Scheme 2*: 3-, 5-, 6-, and 8-position) are in the range $\delta$ 6.0–8.0 ppm. However, methyl protons of MMA and MA lie between $\delta$ 3.4–3.8 ppm, whereas methylene protons (next to ester) of EA and BA lie around $\delta$ 4.0 ppm. The peak areas of these protons are employed to calculate the comonomer composition of the copolymers. The $^1H$ n.m.r. spectrum of P4 is shown in *Figure 1*.

Various methods have been used to obtain MMRs from the copolymer composition data[24]. The method most often used involves a rearrangement of the copolymer composition equation into a form linear in MRRs. For example, in the Fineman-Ross method[25] and the linear form is $G = r_1F - r_2$, where $G = X(Y-1)$, $F = X^2/Y$, $X = [M_1]/[M_2]$, and $Y = d[M_1]/d[M_2]$. $G$ is plotted against $F$ to yield a straight line with slope $r_1$ and intercept $-r_2$. In the Kelen–Tüdos method[26], the linear form is refined by introducing an arbitrary constant $A$ to spread the data more evenly so as to give equal weighting to all data points. Their results are expressed in the form of $T = P(r_1 + r_2/A) - r_2/A$, where $T = G/(A+F)$, $P = F/(A+F)$, $A = (F_mF_M)^{1/2}$, $F_m$ and $F_M$ are the lowest and highest $F$ values, respectively.

The feed and the corresponding copolymer composition at low conversion (<5%) for $M_1$–MMA, $M_1$–MA, $M_1$–EA, and $M_1$–BA comonomer pairs are summarized in *Tables 2–5*. Using the data in *Tables 2–5*, the monomer reactivity ratios can be easily estimated by the Fineman–Ross and Kelen–Tüdos methods. For

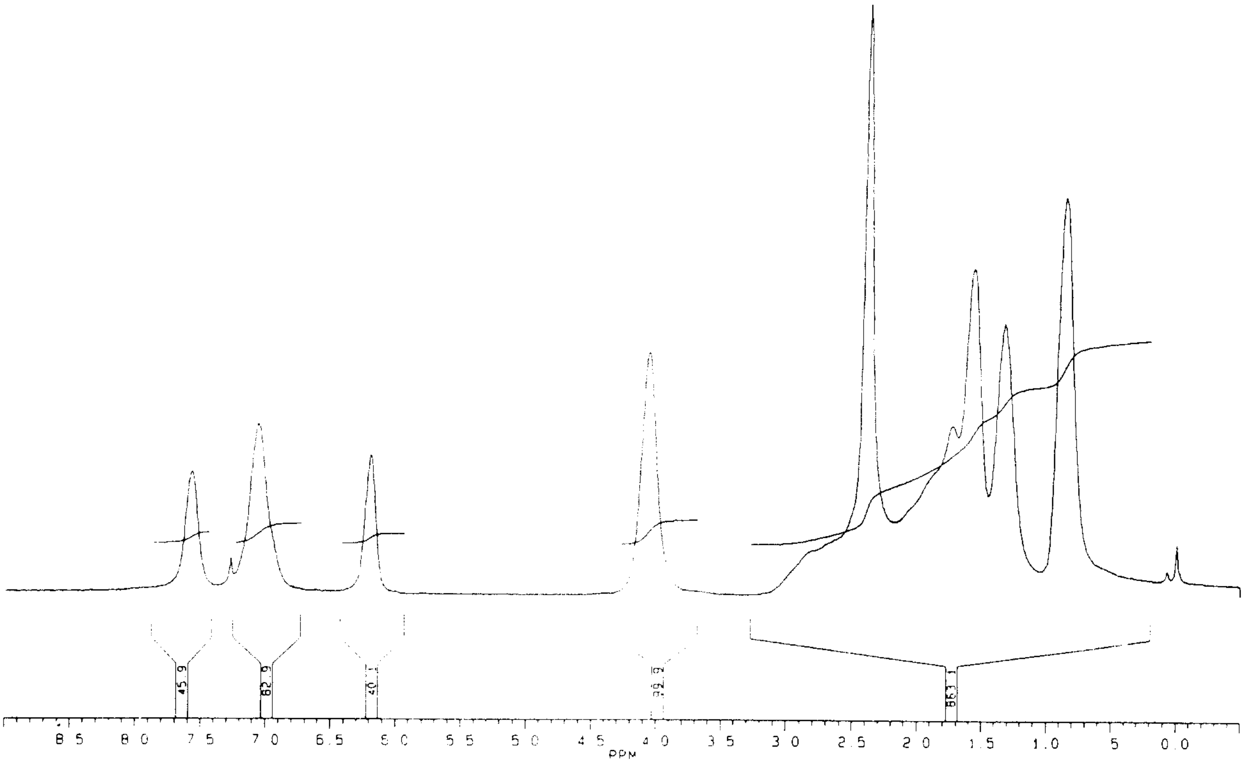


**Figure 1** $^1H$ n.m.r. spectra in $CDCl_3$ of copolymer P4 derived from $M_1$ and BA

**Table 3** Copolymerization of $M_1$ with MA[a]

| Monomer composition (mol%) | | Copolymer yield (%) | Viscosity[b] $\eta_{red}$ (dl g$^{-1}$) | Copolymer[c] composition (mol%) | |
|---|---|---|---|---|---|
| $M_1$ | MA | | | $M_1$ | MA |
| 30.05 | 69.95 | 4.3 | 0.18 | 47.6 | 52.4 |
| 32.82 | 67.18 | 4.3 | 0.17 | 51.2 | 48.8 |
| 39.1 | 60.9 | 1.6 | – | 57.1 | 42.9 |
| 49.8 | 50.2 | 4.9 | 0.19 | 68.3 | 31.7 |
| 50 | 50 | 3.5 | 0.22 | 66.9 | 33.1 |
| 61.43 | 38.57 | 5.2 | 0.23 | 77.5 | 22.5 |
| 75.14 | 24.86 | 5.1 | 0.22 | 86.7 | 13.3 |

[a] Copolymerized in DMF at 65°C using AIBN as initiator
[b] Measured at 0.30 g dl$^{-1}$ chloroform at 30°C
[c] The compositions were calculated from the peak areas of $^1H$ n.m.r. spectra

**Table 4** Copolymerization of $M_1$ with EA[a]

| Monomer composition (mol%) | | Copolymer yield (%) | Viscosity[b] $\eta_{red}$ (dl g$^{-1}$) | Copolymer[c] composition (mol%) | |
|---|---|---|---|---|---|
| $M_1$ | EA | | | $M_1$ | EA |
| 0.58 | 99.42 | 3.8 | 0.22 | 1.2 | 98.8 |
| 26.06 | 73.94 | 4.6 | 0.24 | 43.2 | 56.9 |
| 33.46 | 66.54 | 4.8 | 0.21 | 50.3 | 49.7 |
| 38.32 | 61.68 | 4.9 | 0.19 | 60.4 | 39.7 |
| 39.91 | 60.09 | 3.6 | 0.18 | 58.5 | 41.5 |
| 52.26 | 47.74 | 4.4 | 0.20 | 70.6 | 29.4 |
| 61.03 | 38.97 | 3.2 | 0.21 | 75.5 | 24.5 |

[a] Copolymerized in DMF at 65°C using AIBN as initiator
[b] Measured at 0.30 g dl$^{-1}$ chloroform at 30°C
[c] The compositions were calculated from the peak areas of $^1H$ n.m.r. spectra

**Table 5** Copolymerization of $M_1$ with BA[a]

| Monomer composition (mol%) | | Copolymer yield (%) | Viscosity[b] $\eta_{red}$ (dl g$^{-1}$) | Copolymer[c] composition (mol%) | |
|---|---|---|---|---|---|
| $M_1$ | BA | | | $M_1$ | BA |
| 19.86 | 80.14 | 4.6 | 0.21 | 31.2 | 68.8 |
| 25.30 | 74.70 | 2.8 | | 40.4 | 59.6 |
| 31.68 | 68.32 | 3.4 | 0.26 | 45.6 | 54.4 |
| 32.75 | 67.25 | 3.7 | 0.24 | 45.8 | 54.2 |
| 36.93 | 63.07 | 4.3 | 0.21 | 53.3 | 46.8 |
| 51.00 | 49.00 | 3.1 | | 64.2 | 35.9 |
| 53.31 | 46.49 | 3.4 | 0.21 | 67.9 | 33.2 |
| 81.87 | 18.13 | 3.6 | 0.23 | 89.3 | 10.7 |

[a] Copolymerized in DMF at 65°C using AIBN as initiator
[b] Measured at 0.30 g dl$^{-1}$ chloroform at 30°C
[c] The compositions were calculated from the peak areas of $^1H$ n.m.r. spectra

**Table 6** MRRs in copolymerization of $M_1$ and acrylates

| | Fineman–Ross | | Kelen–Tüdos | | Average | | | |
|---|---|---|---|---|---|---|---|---|
| System | $r_1$ | $r_2$ | $r_1$ | $r_2$ | $r_1$ | $r_2$ | $r_1r_2$ | $1/r_1$ |
| $M_1$–MMA | 0.44 | 1.67 | 0.45 | 1.69 | 0.45 | 1.68 | 0.76 | 2.22 |
| $M_1$–MA | 2.17 | 0.49 | 2.14 | 0.47 | 2.16 | 0.48 | 1.04 | 0.46 |
| $M_1$–EA | 1.97 | 0.40 | 2.11 | 0.44 | 2.04 | 0.42 | 0.86 | 0.49 |
| $M_1$–BA | 1.84 | 0.54 | 1.8 | 0.52 | 1.82 | 0.53 | 0.96 | 0.55 |

example, the results of the $M_1$/MA system are shown in *Figures 2* and *3* by the Fineman–Ross and Kelen–Tüdos methods, respectively. Other systems are also calculated by the same procedures and the results are summarized in *Table 6*. The MRRs of $M_1$ ($r_1 = 2.14$–$2.17$) are much greater than those of MA ($r_2 = 0.47$–$0.49$). It is ideal copolymerization, from the fact that $r_1r_2$ value is near 1.0, and clearly $M_1$ is much more reactive than MA. The $r_1$ values of $M_1$ are greater than those of acrylates ($M_2$) except MMA. The relative reactivity of monomers and their corresponding radicals can be obtained from an analysis of the MRRs[27]. The reactivity of a monomer can

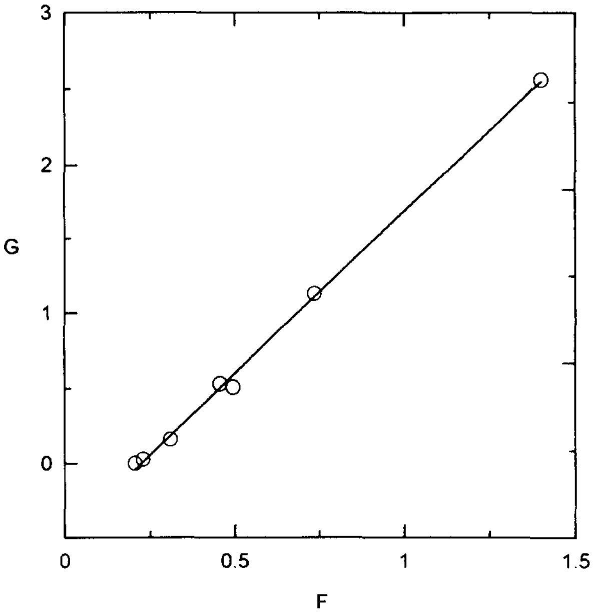


**Figure 2** Determination of MRRs by Fineman–Ross plot for $M_1$–MA

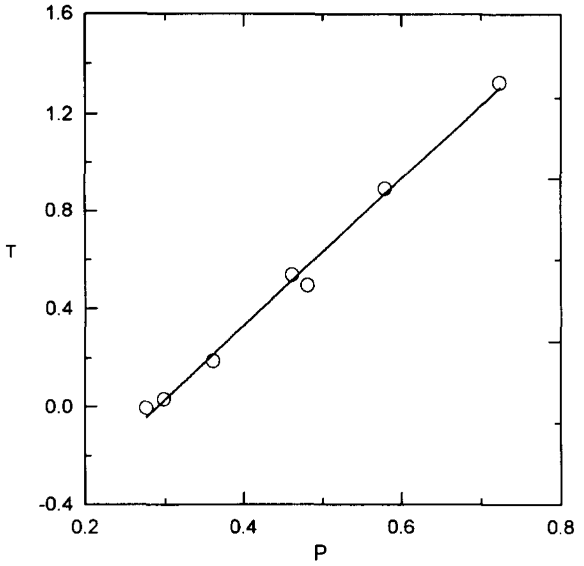


**Figure 3** Determination of MRRs by Kelen–Tüdos plot for $M_1$–MA

be seen by considering the inverse of the MRR ($1/r_1$). This gives the ratio of the rate of reaction of a radical with another monomer to its rate of reaction with its own monomer (for example: $1/r_1 = k_{12}/k_{11}$). The last column of *Table 6* shows $1/r_1$ calculated from the average $r_1$. It shows the relative reactivity of acrylates toward the same propagating radical terminated with $M_1$. Clearly, the reactivity order of the acrylates is MMA > $M_1$ > BA > EA > MA.

The behaviour of vinyl and acrylate monomers with the chemical structure $CH_2{=}CR_1R_2$ in polymerization is affected by the polar character of the olefinic double bond and resonance effects associated with the electronegativity of the substituents $R_1$ and $R_2$, as well as by steric hindrance of these groups in the polymerization steps[28,29]. In this work, the monomers are 1-substituted vinyl monomers, except MMA which is 1,1-disubstituted instead. 4-Methylcoumarin chromophore is the bulkiest substituent in these monomers. However, from the order of reactivity MMA > $M_1$ > BA > EA > MA, clearly the steric effect plays little role in determining the reactivities of these monomers. This result coincides with that of Tamikado *et al.*, who find that the length of side groups of acrylates exerts little influence on their radical copolymerization reactivity with acrylonitrile[30].

*Resonance factors*

The order of monomer reactivity corresponds to the order of increased resonance stabilization by the particular substituent of the radical formed from the monomer[27]. Substituents composed of unsaturated linkage are more effective in stabilizing the radicals because of the loosely held π-electrons, which are available for resonance stabilization. $M_1$, MMA, MA, EA, and BA are all acrylate monomers and possess C=O resonance. However, MMA gets extra stabilization by hyperconjugating with α-methyl protons and, therefore, shows the greatest reactivity. But the reactivity order of $M_1$ > BA > EA > MA cannot be explained by resonance effect because they both contain one C=O resonance linkage.

**Table 7** $^{13}C$ n.m.r. chemical shift of the β-carbon in the monomers

| Monomer | $M_1$ | MA | EA | BA | MMA |
|---|---|---|---|---|---|
| Chemical shift (ppm) | 133.65 | 127.84 | 128.54 | 130.36 | 124.85 |

*Polarization factors*

The reactivity of monomer and radical in free radical polymerization can be analysed in terms of charge density at the β-carbon[31]. On the other hand, the $^{13}C$ n.m.r. chemical shift of the β-carbon of vinyl groups has been reported to be mainly controlled by the π-electron density[32,33], which is closely related to the reactivity of the vinyl compounds. At lower electron density of the β-carbon of the monomer leads to an easier electron transfer from the polymer radical to the monomer and consequently a higher monomer reactivity[34]. The $^{13}C$ n.m.r. spectra of $M_1$, MMA, and EA are shown in *Figure 4* and the chemical shifts of the β-carbon of all monomers are summarized in *Table 7*. Clearly, values of the chemical shifts are in the order of $M_1$ > BA > EA > MA > MMA, signifying that the electron density of the β-carbon is in the order of MMA > MA > EA > BA > $M_1$. Therefore, the monomer reactivity order should be as $M_1$ > BA > EA > MA with the exception of MMA. Although MMA possesses the highest electron density, its reactivity is still greater than other monomers. This can be explained by its extra stabilization through hypreconjugation of the α-methyl group to the radical centre.

*Thermal properties of the copolymers*

The segmental mobility of the polymer main chain plays an important role in determining the photocrosslinking rate of photosensitive polymers, i.e. greater

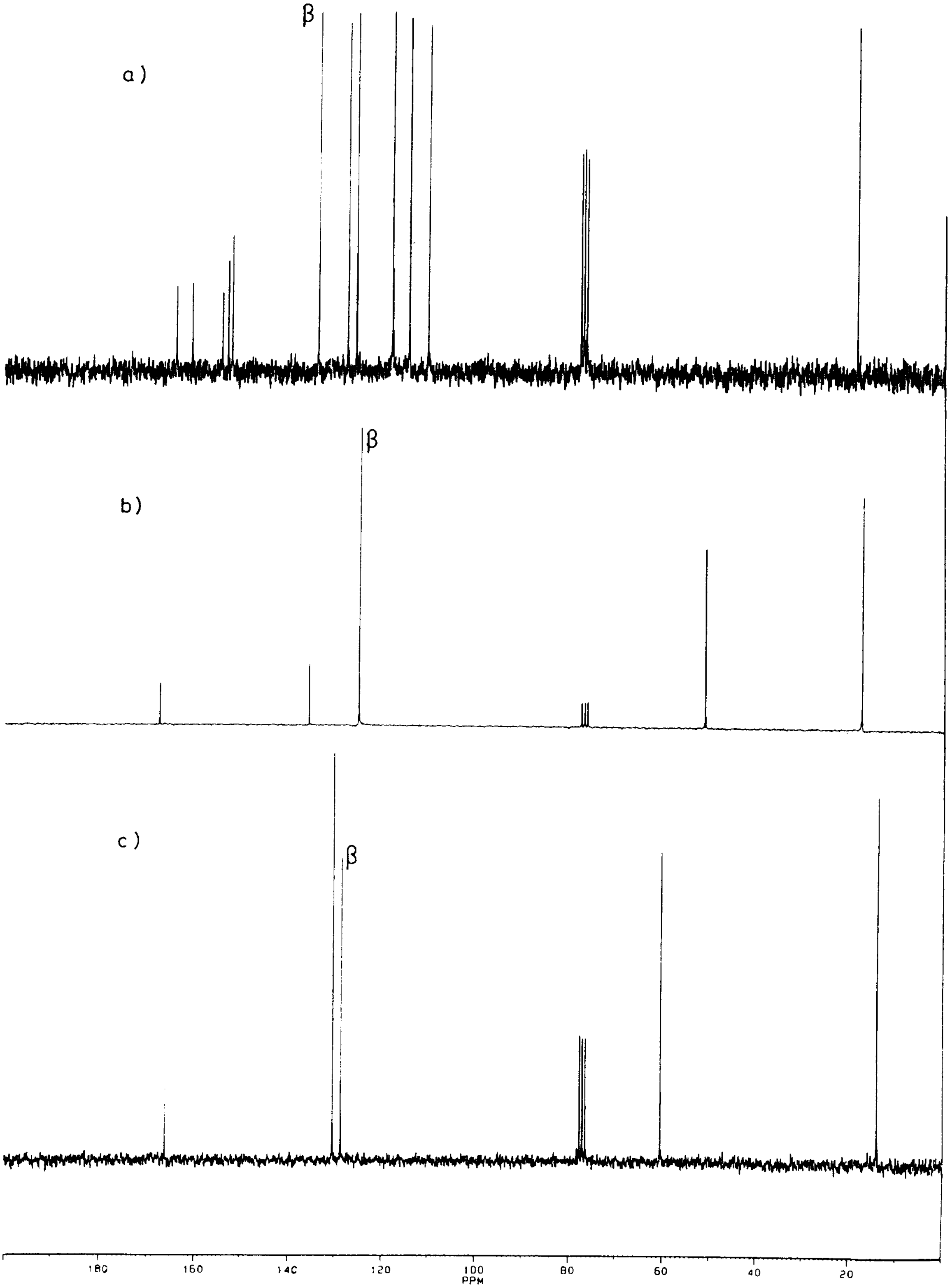


**Figure 4** $^{13}$C n.m.r. spectra of $M_1$, MMA, and EA

mobility renders faster reaction attributable to easy approach of photoreactive chromophores. The mobility of the main chain is mainly influenced by its chemical structure. The glass transition temperature ($T_g$) is a useful threshold temperature above which cooperated segmental motions of the main chain are possible. In this work, differential scanning calorimetry (d.s.c.) was employed to determine the $T_g$s of copolymers with the

**Table 8** $T_g$ of copolymers P1–P4 and homopolymer of 7-acryloyloxy-4-methylcoumarin ($PM_1$)[a]

| | Composition (mol%) | | |
|---|---|---|---|
| Polymers ($M_1$–$M_2$) | $M_1$ | $M_2$ | $T_g$ (°C) |
| $PM_1$ | 100 | | 122.1 |
| P1 ($M_1$–MMA)[b] | 26.1 | 73.9 | 112.1 |
| P2 ($M_1$–MA)[b] | 11.2 | 88.8 | 13.5 |
| P3 ($M_1$–EA)[b] | 1.3 | 98.7 | −17.6 |
| | 43.1 | 56.9 | 66.3 |
| P4 ($M_1$–BA)[b] | 33.3 | 66.7 | 2.1 |
| | 61.1 | 38.9 | 39.6 |
| | 66.0 | 34.0 | 41.5 |

[a] Determined by d.s.c. Heating rate: 20°C $min^{-1}$ under nitrogen flow

[b] Prepared by radical copolymerization in DMF at 65°C for 6 h

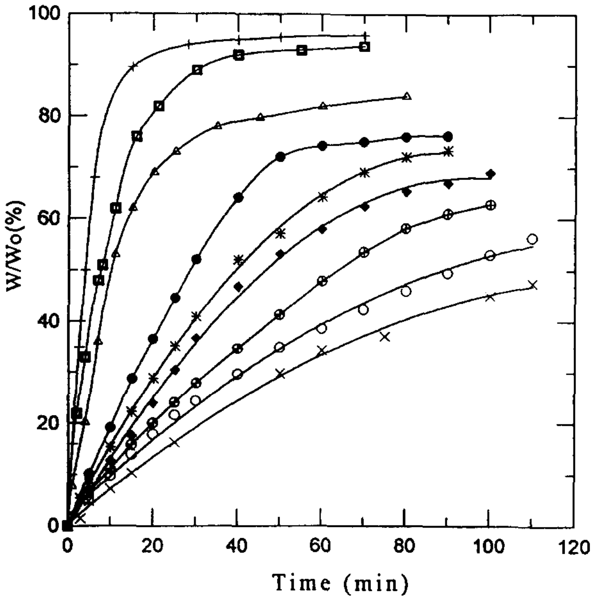
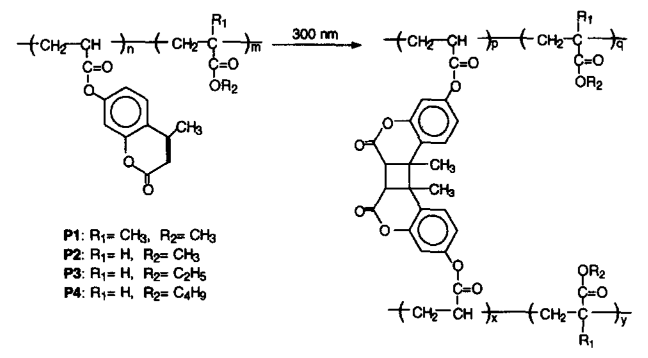


**Figure 5** Characteristic curves of copolymers P3 and P4. $W$ is the height of the film after irradiation with 300 nm light followed by developing in chloroform, whereas $W_0$ is the weight before irradiation. P4 with BA content: 66.7% (+), 54.4% (□), and 45.5% (Δ); P3 with EA content: 56.9% (●), 49.3% (*), 41.5% (◆), 29.4% (⊕), 24.5% (○), and 14.2% (×)

different compositions. The copolymers and homopolymer used in thermal analysis were prepared by the same procedures mentioned above. The $T_g$s of $PM_1$ and copolymers are summarized in Table 8. Homopolymer of $M_1$ possesses the highest $T_g$ (122.1°C) due to the bulky and rigid 4-methylcoumarin chromophores. Therefore, $T_g$s of the homopolyacrylates are in the order of 122.1($PM_1$) > 104.9°C (PMMA) > 9.9°C (PMA) > −24.2°C (PEA) > −54.2°C (PBA)[35].

As shown in *Table 8*, the $T_g$s of the copolymers can be controlled by changing the mol% of $M_1$, i.e. the lower the $M_1$ content and the longer the side chain, the lower the $T_g$. However, for application as photosensitive polymers, the content of photoreactive comonomer ($M_1$) should not be too low. That means the most suitable comonomers are BA and EA. Although the $T_g$s of the copolymers with EA can be lower than room temperature (−17.6°C; EA = 98.7%), the content of photoreactive $M_1$ residue is only 1.3%. Therefore, from a practical point of view, the best comonomer would be BA from this study, and its content would be in the region of 30–80%.



Scheme 3

*Characteristic curves of copolymers P3–P4* (Scheme 3)

Photosensitivity of negative-type photoresist, such as polyvinyl cinnamate, has been evaluated by its characteristic curve. The characteristics curve is established by plotting $W/W_0$ with irradiation time[36] ($W_0$ is the film weight before exposing 300 nm light, whereas $W$ is the residual weight after exposure followed with development in chloroform for 30 min). $W/W_0$ can be used to depict the fraction of crosslinking after irradiation. As shown in *Figure 5*, for copolymers P3 and P4, both asymptotic $W/W_0$ and photocrosslinking rate increase with increasing content of EA and BA, respectively. This can be attributed to the increasing chain mobility which promotes the translational and rotational motion of the photoreactive 4-methylcoumarin chromophores. Accordingly, the possibility for two 4-methylcoumarin groups to approach each other is increased with increasing EA and BA concentration for P3 and P4, respectively. However, the asymptotic $W/W_0$ values of P4 with 66.7% BA and 54.4% BA are ca. 96% and 93%, respectively, but the greatest asymptotic $W/W_0$ of P3 is only 76%. The asymptotic $W/W_0$ values of P4 are much greater than those of P3. Moreover, the initial slopes of the curves also show the same trend, indicating that photosensitivity of P4 is higher than P3.

As mentioned above, the crosslinking rates and ultimate $W/W_0$ are mainly determined by the content of $M_2$, although 4-methylcoumarins of $M_1$ are the real reaction sites. For example, for P1 both crosslinking rate and ultimate $W/W_0$ increase as BA content is increased from 45.5% to 66.7% (*Figure 5*), while they decrease with increasing $M_1$ content. This means that the mobility of the copolymer main chain plays a dominant role in determining the photoreactivity of copolymers P3 and P4. The $T_g$ of P4 with 66.7% BA is 2.1°C as shown in *Table 8*, whereas those of P3 are greater than 66.3°C ($T_g$ of P3 with 56.9% EA). Although the $T_g$ of P3 can be lowered furthermore by increasing EA concentration, the content of photoreactive 4-methylcoumarin groups will be decreased significantly. Therefore, it is concluded that, from copolymers studied, the copolyacrylates containing BA (P4) are the better negative-type photoresist materials for practical applications.

## CONCLUSION

Photosensitive copolyacrylates were successfully prepared from radical copolymerization of $M_1$ with various acrylates ($M_2$: MMA, MA, EA, BA), using AIBN as initiator. The reduced viscosities are in the range of 0.17–0.26 dl g$^{-1}$ ($c = 0.3$ g dl$^{-1}$ chloroform at 30°C). The MRRs of the four comonomer pairs were determined by the Fineman–Ross and Kelen–Tüdos methods: $r_1 = 0.45$, $r_2 = 1.68$ for $M_1$–MMA; $r_1 = 2.16$, $r_2 = 0.48$ for $M_1$–MA; $r_1 = 2.04$, $r_2 = 0.42$ for $M_1$–EA; $r_1 = 1.82$, $r_2 = 0.53$ for $M_1$–BA. The $T_g$s of the copolymers were determined by d.s.c. Incorporation of $M_1$ increases the $T_g$s of the copolymers, which can be ascribed to the bulkiness and rigidity of 4-methylcoumarin chromophores. Irradiation of the copolymers in the film state by 300 nm u.v. light renders dimerization of the pendant 4-methylcoumarin groups and results in gradual crosslinking. From their characteristic curves, it is found that the rate and ultimate fraction of crosslinking depends mainly on and increase with chain mobility of the copolyacrylates. The $T_g$ of copolyacrylates P4 can be controlled to be lower than room temperature by increasing concentration of BA easily, while this manipulation in P3 with EA will result in significant decrease in content of photoreactive 4-methylcoumarin chromophore. Therefore, the copolyacrylates with BA are the better negative-type photoresist materials than those containing MMA/EA/MA.

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