

# The group transfer copolymerization of alkyl acrylates with acrylates containing electron-donor or -acceptor substituents

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*N*-(2-Hydroxyethyl)carbazolyl acrylate, an electron-donor monomer, or 2-(trimethylsiloxy)ethyl acrylate were copolymerized with methyl acrylate and with *n*-butyl acrylate, respectively, via group transfer polymerization in tetrahydrofuran. By polymer analogue transformations the trimethylsilyl groups were substituted by 3,5-dinitrobenzoyl groups to get the corresponding electron-acceptor ( $\beta$ -hydroxyethyl)-3,5-dinitrobenzoyl acrylate copolymers. The content of the electron-donor (respectively of the electron-acceptor) groups in the acrylate copolymers was in the range of up to 10 mol%. The thermal behaviour of these copolymers obtained via group transfer polymerization is compared with that of the corresponding copolymers obtained by radical copolymerization.

(Keywords: group transfer; copolymerization; electron-donor or electron-acceptor copolymers; glass transition)

## INTRODUCTION

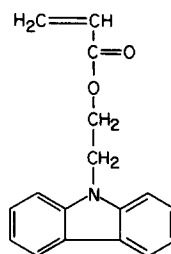
Monodisperse polymers with the desired molecular weights in the range of 1000 to 20 000 g mol<sup>-1</sup> of polar aprotic monomers, i.e. methyl methacrylate, were synthesized at ambient temperatures via group transfer polymerization (GTP), a new insertion polymerization technique<sup>1</sup>. Initiation occurred using ketene silyl acetals in the presence of a nucleophilic (e.g. HF<sub>2</sub><sup>-</sup>, CN<sup>-</sup>, F<sup>-</sup>, N<sub>2</sub><sup>-</sup>) or electrophilic (Lewis acid) catalyst.

Besides the homopolymerization of methacrylates, acrylates, acrylamides, maleimides, butyrolactones, etc., the preparation of block copolymers of controlled sequence length, of telechelic polymers with hydroxy or carboxy end-groups and of statistical random copolymers illustrates the multiple synthetic possibilities of GTP<sup>2-5</sup>. Methacrylic polymers with reactive pendant functional groups like hydroxy groups are accessible only via polymerization of protected monomers, for instance 2-(trimethylsiloxy)ethyl methacrylate, followed by the corresponding polymer analogue transformation<sup>5</sup>.

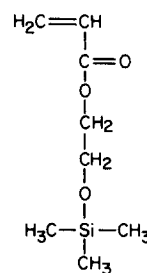
To study the influence on thermal and rheological properties of donor-acceptor (DA) interactions in immiscible/miscible polymer acrylate blends, we were interested in the synthesis of copolymers of methyl and *n*-butyl acrylate, respectively, containing up to 10 mol% pendant electron-donor (carbazolyl) or electron-acceptor (3,5-dinitrobenzoyl) groups.

In this first paper are presented the synthesis of the monomers *N*-(2-hydroxyethyl)carbazolyl acrylate (I) and 2-(trimethylsiloxy)ethyl acrylate (II) and their group transfer copolymerization with either methyl acrylate or *n*-butyl acrylate. Taking into account the impossibility of direct copolymerization of the electron acceptor ( $\beta$ -hydroxyethyl)-3,5-dinitrobenzoyl acrylate (III), the respective copolymers were then obtained via polymer

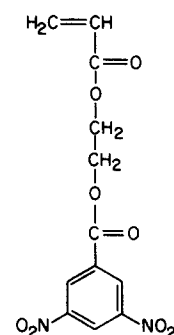
analogue transformations of the 2-(trimethylsiloxy)ethyl acrylate copolymers.



(I)



(II)



(III)

## EXPERIMENTAL

### Materials

Methyl acrylate (MA) and *n*-butyl acrylate (BA) of PA grade (Fluka) were freshly redistilled before use in nitrogen atmosphere in the presence of CaH<sub>2</sub> and Cu(I)Cl.

The electron donor *N*-(2-hydroxyethyl)carbazolyl acrylate (HECA)<sup>6</sup> was synthesized and purified in accordance with the literature and then recrystallized several times from hexane to assure the absence of proton-donating species.

2-Hydroxyethyl acrylate (HEA) 97% (Aldrich), the precursor of ASi, was purified by passage through a column of silica gel 60 of 0.2–0.5 mm (35–70 mesh ASTM) using diethyl ether/petroleum ether (40/60) 1:1 as eluent.

2-(Trimethylsiloxy)ethyl acrylate (ASi) was prepared in the following way. HEA (50 g, 0.430 mol) was dissolved in a mixture of 150 ml dry pyridine and 132 ml hexamethyldisilazane (0.626 mol) in nitrogen atmosphere.

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Redistilled trimethylchlorosilane (76.2 ml, 0.600 mol) were slowly added under stirring. The mixture was subsequently stirred for 10 h at 25°C. Filtration followed by distillation in nitrogen atmosphere through a Vigreux column (1 × 13 cm) at 39–40°C and 60.0 Pa in the presence of Cu(I)Cl gave pure colourless liquid ASi (checked by t.l.c.) (69.6 g, yield 86%).

$n_D^{25} = 1.4265$  (lit.<sup>7</sup>  $n_D^{25} = 1.4260$ ). <sup>1</sup>H n.m.r. ( $\bar{C}DCl_3$ /TMS, RT) (ppm): 0.15 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 3.83 (t, 2H, –CH<sub>2</sub>–O–Si), 4.25 (t, 2H, C–O–CH<sub>2</sub>–), 5.63–6.61 (m, 3H, CH<sub>2</sub>=CH–). I.r. (cm<sup>-1</sup>): 740, 835+1240 (vs, Si–CH<sub>3</sub>, vl/rocking band), 1095 (vs, Si–O, vl). Elemental analysis: found C 51.33%, H 8.62%; calculated C 51.03%, H 8.67%.

The initiator 1-methoxy-2-methyl-1-(trimethylsilyloxy)-1-propene 95% (Aldrich) was used as received.

Tris(dimethylamino)sulphonium bifluoride (TASHF<sub>2</sub>) used as catalyst was prepared starting from tris(dimethylamino)sulphonium (trimethylsilyl)difluoride (Aldrich) in dry acetonitrile by addition of 0.5 mol water and stirring. The acetonitrile was removed under reduced pressure and the colourless solid TASHF<sub>2</sub> was obtained by drying for 3 days at room temperature and 0.133 Pa. The product was stored under argon.

Tetrahydrofuran (THF) used as polymerization solvent was refluxed over potassium and distilled under argon.

All other reagents were used as received.

#### Group transfer copolymerization

Copolymerization was carried out under argon in polymerization flasks equipped with a thermometer. Connected on a high-vacuum line the flasks were immersed in a water/ice bath. A syringe technique was used for the introduction of liquid reactants and solvents. All glassware was dried at 200°C for at least 4 h before use.

The copolymerization was conducted by a batch process in which the catalyst was added to the solution of THF, monomers and initiator.

In a representative copolymerization experiment the freshly dried solvent THF (over MgBu<sub>2</sub>) was condensed in the polymerization flask. Then the comonomers HECA and MA (or BA) or ASi and MA (or BA) (total mass 8 g) were added in imposed concentration ratios and after injecting the initiator (in amount required by the desired polymerization degree) the reaction mixture was stirred until complete dissolution.

Tris(dimethylamino)sulphonium bifluoride (~0.1 mol% relative to initiator) was then added to the homogeneous solution and the start of the copolymerization was followed by the increase of the temperature up to 30–40°C. The reaction mixture was subsequently cooled and stirred for 3–3.5 h at 25–30°C. The copolymer was then poured into methanol and purified by several precipitations from CHCl<sub>3</sub> solution into methanol.

During the copolymerization of ASi and MA (or BA) the temperature rose up to 50°C before it became controllable between 20 and 30°C. The reaction time was as long as 15 h.

#### Polymer analogue transformations

Synthesis of poly(methyl or n-butyl acrylate-co-(3,5-dinitrobenzoyl)ethyl acrylate) (poly(MA/BA-co-DNBA)) was by polymer analogue transformations of poly(MA/BA-co-ASi).

*Cleavage of the trimethylsilyl groups and formation of the copolymer poly(MA/BA-co-AOH).* The solution of 4 g poly(MA-co-ASi) (7.4 mol% ASi) in 35 ml dry THF was refluxed for 1.5 h with 6 ml of methanol and 1 ml of tetrabutylammonium fluoride (1 M in THF). The solvent was removed by evaporation. The product obtained was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, washed with water and dried (MgSO<sub>4</sub>). After solvent evaporation the copolymer was reprecipitated several times from THF with methanol to give 3.3 g (82.5% yield) of the desired copolymer. This is confirmed by the absence of protons characteristic of the trimethylsilyl group in <sup>1</sup>H n.m.r.

*Esterification of the alcohol groups and formation of the copolymer poly(MA/BA-co-DNBA).* To the solution of 3 g poly(MA-co-AOH) (containing 7.4 mol% hydroxyl groups) and 1.05 ml dry triethylamine (7.54 mmol) in 40 ml of dry CH<sub>2</sub>Cl<sub>2</sub> at ice-bath temperature was added dropwise over 20 min with stirring a solution of 1.774 g 3,5-dinitrobenzoyl chloride (Fluka, 98%) (7.54 mmol, i.e. three times the number of moles of hydroxyl groups in the precursor copolymer) in 35 ml of dry CH<sub>2</sub>Cl<sub>2</sub>. The stirring was continued for 7.5 h at RT. After removing the triethylamine hydrochloride by filtration, the resulting copolymer was poured into methanol/toluene 3:1. The precipitate was then reprecipitated twice from THF into the methanol/toluene mixture and then into pure methanol, giving 2.73 g yellow poly(MA-co-DNBA) (91% yield). The reaction was quantitative as confirmed in the i.r. spectrum by the disappearance of the absorption bands of the hydroxyl groups (3550 and 1055 cm<sup>-1</sup>). The ASi content before reaction was in good agreement with the content of the DNBA groups after the transformation measured by <sup>1</sup>H n.m.r. Also the molecular weight of the copolymer increased correspondingly.

#### Techniques

The contents of HECA and DNBA, respectively, in the copolymers were measured by <sup>1</sup>H n.m.r. spectroscopy (Bruker WP 80 CW or Bruker Pulse CXP 90). I.r. measurements were performed using polymer films on NaCl plates (Perkin-Elmer 1330 IR spectrophotometer). Molecular weights were determined by g.p.c. in THF, using polystyrene standards for calibration. Glass transition temperatures ( $T_g$ ) were measured using the Perkin-Elmer DSC-7 differential scanning calorimeter. After a first controlled heating-cooling cycle, d.s.c. scans were run using heating rates of 10, 20, 30 and often 40°C min<sup>-1</sup>. Temperatures  $T_g$  measured by the inflection point of the d.s.c. curves were then extrapolated to zero heating rate.

## RESULTS AND DISCUSSION

In Table 1 are shown the copolymerization data and the characteristics of the studied copolymers MA-co-HECA, BA-co-HECA, MA-co-DNBA and BA-co-DNBA. It was demonstrated for homopolymerization of both *N*-(2-hydroxyethyl)carbazolyl methacrylate and *N*-ethyl-3-hydroxymethylcarbazolyl methacrylate that the GTP method combines the important advantages of 'living' polymerization, i.e. narrow molecular-weight distribution and control of the molecular weight<sup>8</sup>. According to equation (1) there are two possible ways for increasing the molecular weight, either by increasing the monomer concentration or by reducing the initiator concentration:

$$P_n = [\text{monomer}]/[\text{initiator}] \quad (1)$$

**Table 1** Copolymerization data and characteristics of the copolymers

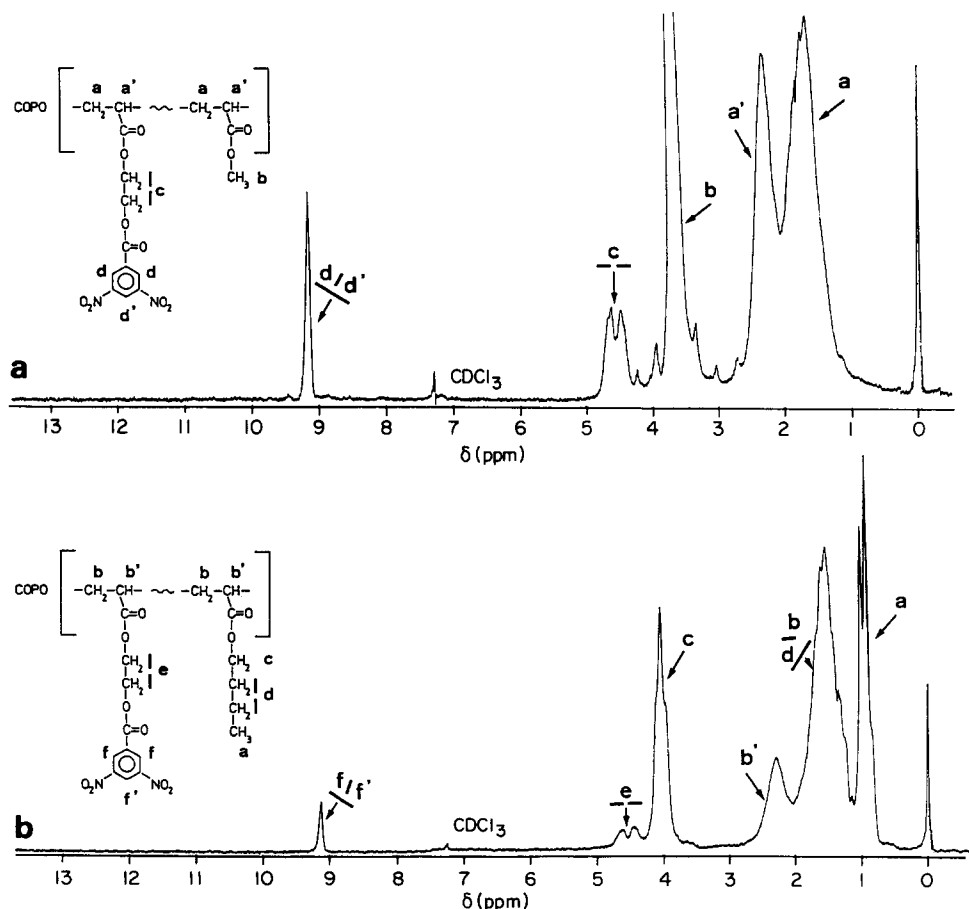
No.	Monomer (mol l <sup>-1</sup> )	Initiator (mmol l <sup>-1</sup> )	Conversion (wt%)	Content HECA or ASi, DNBA <sup>a</sup> [n.m.r.] (mol%)	Reaction time (h)	$\bar{M}_n \times 10^{-3}$ [theory] (g mol <sup>-1</sup> )	$\bar{M}_n \times 10^{-3}$ [g.p.c. (RI) <sup>b</sup> ] (g mol <sup>-1</sup> )	$U = \frac{M_w}{M_n} - 1$	$T_g^c$ [DSC-7] (K)
Copolymers with donor:									
MA-co-HECA ( $X = 15$ ) <sup>d</sup>									
1	2.442	12.50	60	9.4	3	20	4.94	0.45	—
2	2.442	6.25	64	9.6	3.5	40	5.16	0.48	—
3	2.442	4.17	65	10.1	3	60	5.10	0.55	297.7
4	4.884	25.00	80	5.8	3.5	20	5.72	1.49	288.4
5	4.884	12.50	72	4.6	3	40	9.56	1.34	286.9
BA-co-HECA ( $X = 15$ )									
6	3.555	25.00	70	7.2	3	20	5.66	0.81	230.9
7	3.555	12.50	56	8.9	3	40	10.44	2.41	234.3
Copolymers with acceptor:									
MA-co-DNBA ( $X = 10$ )									
8	2.619	12.50	58	7.4	5	20	7.77	1.46	—
MADN				8.1/6.0			18.53	0.92	287.0
9	3.932	7.50	62	8.3	15	50	12.59	1.85	—
MADN				9.3/10.4			30.43	1.57	287.2
10	10.484	20.00	65	6.4	3	50	22.68	0.93	—
MADN				6.7/7.3			37.16	0.81	284.0
BA-co-DNBA ( $X = 10$ )									
11	4.490	12.00	61	7.2	5	50	18.90	1.82	—
12	4.354	11.64	60	6.6	5	50	16.92	1.34	—
BADN				8.3/6.3			27.17	0.96	233.9

<sup>a</sup> N.m.r.: method A proton integral spacer (DNBA) to methyl group (MA/BA); method B proton integral aromatic (DNBA) to methyl group (MA/BA); A/B

<sup>b</sup> G.p.c.: in THF (polystyrene standards) using RI detection; real molecular weights are double these (proved with osmotic measurements)<sup>11</sup>

<sup>c</sup> DSC-7:  $T_g$  values extrapolated to zero heating rate

<sup>d</sup>  $X = [M_1]/[M_2]$  (monomer feed);  $M_1 = \text{MA, BA}$ ;  $M_2 = \text{HECA, ASi}$ . Solvent: THF



**Figure 1** 80 MHz <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>, TMS, RT): (A) poly(MA-co-DNBA) 6.7/7.3 mol% acceptor content; (B) poly(BA-co-DNBA) 8.3/6.3 mol% acceptor content

The analysis of the data shown in Table 1 suggests that the control of the molecular weight by reducing the initiator concentration seems to work only at higher overall initial monomer concentrations (compare for instance Nos. 1 and 2 with 4 and 5, respectively). This is valid also for the BA-co-HECA system. As observed in kinetic studies of the GTP of methyl methacrylate, higher overall monomer concentration favours termination<sup>9</sup>. This may explain the higher polydispersities obtained with the acrylates (see also ref. 5) and the impossibility to realize higher conversions. Simultaneously the degree of insertion of the bulky HECA groups into MA copolymers drops from 10 to about 5 mol% by doubling the initial overall monomer concentration at constant MA/HECA ratio. This suggests that the 'associative' polymerization mechanism seems to be sensitive to steric hindrance.

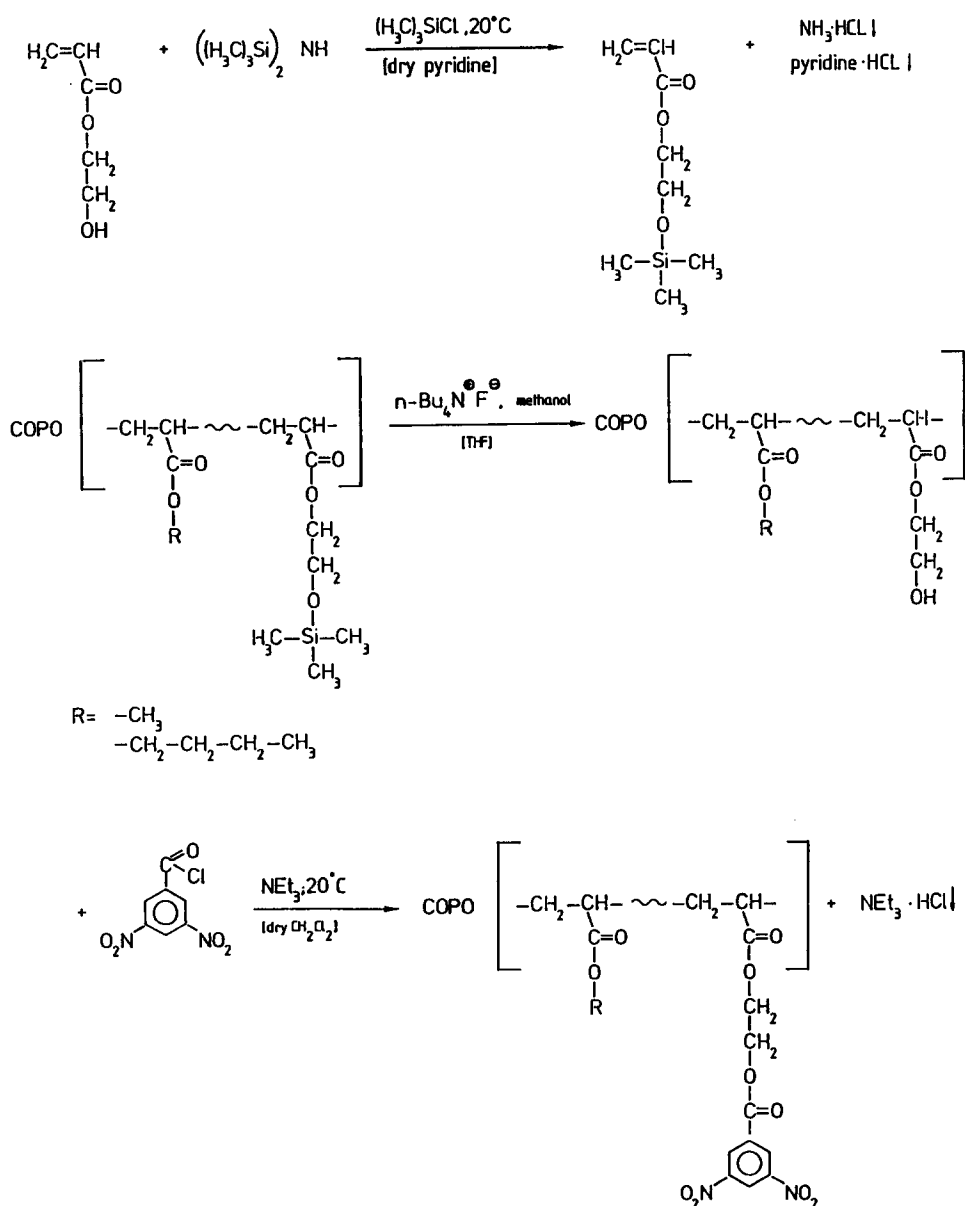
The acceptor copolymers MA-co-DNBA and BA-co-DNBA are not accessible by direct copolymerization due to the ambivalent charge character of the nitro group. To prepare these copolymers by GTP it is necessary to start with the synthesis of the silyl-protected monomer and after copolymerization to apply the polymer analogue transformation techniques:

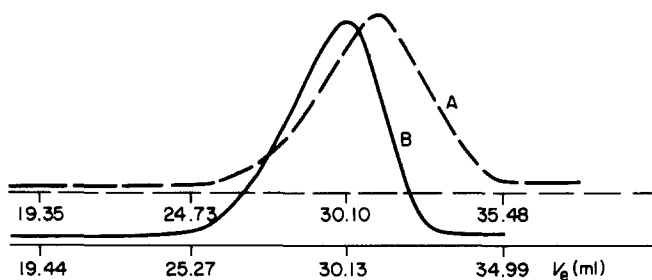
The quantitative transformation is supported by both the absence of the O-H band (vl, 3550 cm<sup>-1</sup>) and the C-O band (C-OH) (vl, 1055 cm<sup>-1</sup>) in the i.r. spectra and by the <sup>1</sup>H n.m.r. (Figure 1). The ratios of the proton integrals of the spacer (DNBA) to the methyl group (MA/BA) – method A – and of the aromatic (DNBA) to the methyl group (MA/BA) – method B – are in good agreement (see Table 1).

The pronounced increase of the molecular weight after transformation cannot be attributed solely to a fractionation effect of the several reprecipitations suggested by the lower polydispersities, but points mainly to the successful transformation (Figure 2).

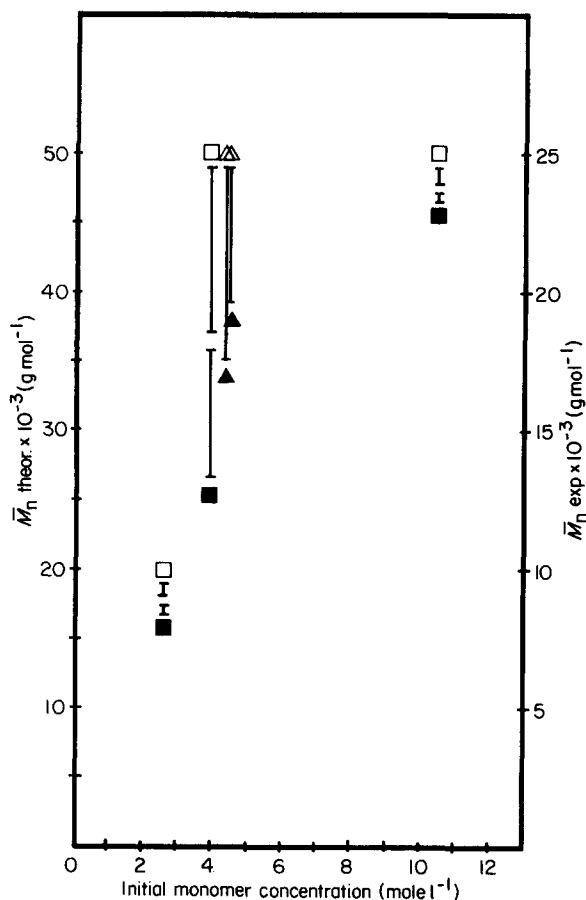
It is remarkable that the actual molecular weights, as determined by g.p.c. (polystyrene), are lower than expected and the polydispersities are almost comparable with those of the copolymers obtained by radical polymerization<sup>10,11</sup>. As indicated before, this is attributed to termination by monomer transfer. Nevertheless, the control of the molecular weight by increasing the initial overall monomer concentration (Nos. 8–10 and 11, 12) seems more obvious than by reducing the initiator concentration (Figure 3).

The copolymerization of MA/BA-co-ASi using bi-





**Figure 2** G.p.c. curves (RI detection/with controlled flow): peak A, poly(MA-co-AOH) 7.4 mol% ( $\bar{M}_n = 7800$ ,  $U = 1.46$ ); peak B, poly(MA-co-DNBA) 8.1/6.0 mol% ( $\bar{M}_n = 18\,500$ ,  $U = 0.92$ )



**Figure 3** Molecular-weight dependence on the initial monomer concentration for: poly(MA-co-ASi), ( $\square$ ) theory, ( $\blacksquare$ ) observed; poly(BA-co-ASi), ( $\triangle$ ) theory, ( $\blacktriangle$ ) observed

fluoride as catalyst is accompanied by the partial cleavage of the protecting trimethylsilyl group. This explains the difficulties in temperature control at the beginning of the GTP. It is also supported by the observation that it was not possible to prepare homopolymers of the ASi monomer.

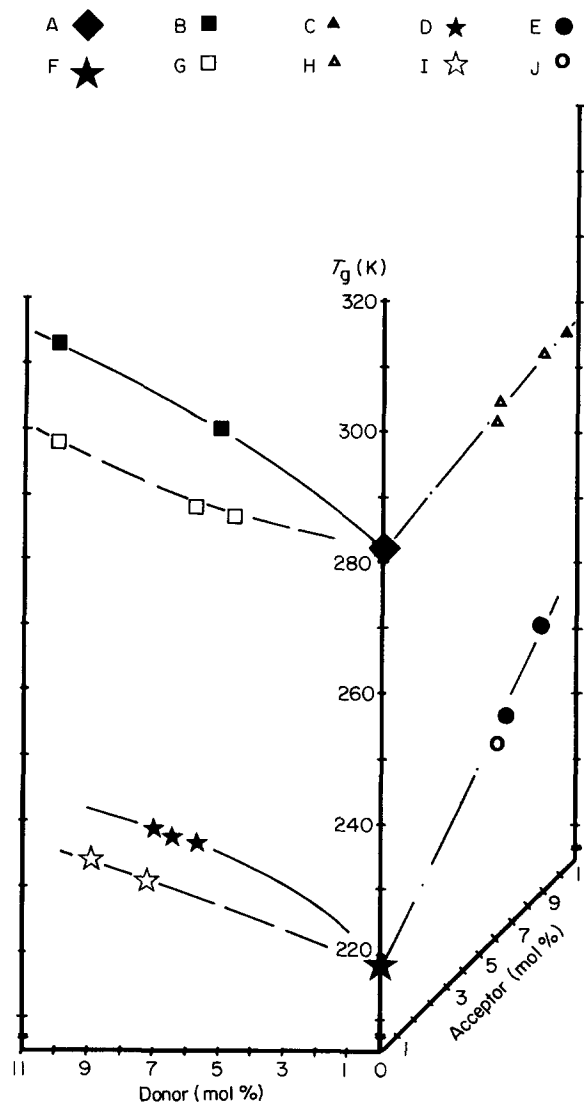
Finally, in Figure 4 are compared the glass transition temperatures of the copolymers obtained by radical copolymerization (see Table 2<sup>11,12</sup>) with those of the copolymers obtained by GTP. The agreement is satisfactory and the somewhat higher  $T_g$  temperatures of the radical HECA copolymers may be explained by their higher molecular weights.

## CONCLUSIONS

Acrylic monomers are copolymerizable with the donor HECA monomer by group transfer polymerization for statistical copolymers of the systems MA-co-HECA and BA-co-HECA, respectively. Acceptor groups containing copolymers of the systems MA-co-DNBA and BA-co-DNBA are accessible only by GTP of a silyl-protected monomer followed by the corresponding polymer analogue transformations. The control of the molecular weight of the copolymers is more efficient by variation of the initial monomer concentration than of the initiator concentration.

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**Figure 4** Comparison of the glass transition temperatures vs. composition data of (a) radical homo- and copolymers (A) poly(methyl acrylate), (B) poly(MA-co-HECA), (C) poly(MA-co-DNBA), (D) poly(BA-co-HECA), (E) poly(BA-co-DNBA), (F) poly(*n*-butyl acrylate), with (b) GTP copolymers (G) poly(MA-co-HECA), (H) poly(MA-co-DNBA), (I) poly(BA-co-HECA), (J) poly(BA-co-DNBA) (for the acceptor copolymers, acceptor content is the arithmetic mean of methods A and B)

Table 2  $T_g$  values of radical homo- and copolymers

Sample	Content of HECA or DNBA [n.m.r. <sup>a</sup> /u.v. <sup>b</sup> ] (mol%)	$\bar{M}_w \times 10^{-3}$ [g.p.c. (RI) <sup>c</sup> ] (g mol <sup>-1</sup> )	$U = \frac{M_w}{M_n} - 1$	$T_g^d$ [DSC-7] (K)
<b>Homopolymers</b>				
MA	—	44.3	0.41	282.4
BA	—	51.4	0.73	218.4
<b>Donor copolymers</b>				
MAHE	5.0 <sup>a</sup>	90.8	2.41	300.3
MAHE	10.2 <sup>a</sup>	33.7	1.91	313.1
BAHE	5.7 <sup>a</sup>	44.6	1.05	237.2
BAHE	6.4 <sup>a</sup>	—	—	238.0
BAHE	7.0 <sup>b</sup>	30.3	1.94	238.8
<b>Acceptor copolymers</b>				
MADN	11.2 <sup>b</sup>	—	—	287.4
BADN	7.7 <sup>b</sup>	65.6	1.55	237.8
BADN	9.9 <sup>b</sup>	58.8	1.71	246.8

<sup>a</sup> N.m.r.: integral ratio aromatic to aliphatic protons

<sup>b</sup> U.v.: extinction coefficients are determined with low-molecular-weight models: *N*(2-hydroxyethyl)carbazolyl acetate and acetyl- $\beta$ -hydroxyethyl-3,5-dinitrobenzoate

<sup>c</sup> G.p.c.: in THF (polystyrene standards) using RI detection

<sup>d</sup> DSC-7:  $T_g$  values extrapolated to zero heating rate

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