Melt Viscosity Characteristics of Methacrylate–Styrene Copolymers

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Synopsis

The activation energies of flow E_A of methacrylate–styrene copolymers containing n-butyl, n-hexyl, n-heptyl, n-octyl, n-decyl, n-dodecyl, n-tridecyl, n-octadecyl, and cyclohexyl methacrylate have been investigated as a function of molecular weight, composition, and methacrylate monomer. Below a critical pendent group molar volume per chain unit (120 ± 10 ml Le Bas units), E_A was found to increase with molar volume; and above this value, a decrease in E_A was observed, reflecting a decrease in copolymer density. Copolymers with pendent group molar volumes per average chain unit of between 96 and 140 ml (Le Bas units) were found to exhibit sufficiently high E_A values to render them suitable for use in thermoplastic and photothermoplastic devices with superior development and erasure rates, at temperatures which enabled the attainment of the development and erasure viscosities with a low expenditure of heat energy. Methacrylate–styrene copolymers with long-chain ester methacrylates (viz., n-decyl and n-dodecyl methacrylate) were found to exhibit critical molecular weights M_c below 3000; and M_c was found to decrease with increasing methacrylate tail length and methacrylate concentration. These M_c values correspond to critical chain lengths Z_c below 45. Similar Z_c values have been previously reported for acrylonitrile–methyl methacrylate copolymers[30] and ethylene–propylene copolymers.[28]

INTRODUCTION

Thermoplastic[1,2] and photothermoplastic[3,4] devices have attracted much attention since the pioneering paper of Glenn,[5] because they offer high-density information storage at high diffraction efficiencies. In such devices an electron beam, or photoconductor switching-in combination with uniform charging of a photoconductive thermoplastic layer[6] or a thermoplastic–photoconductor sandwich,[3,4] is used to induce a charge distribution over the thermoplastic (or photoconductive thermoplastic) layer corresponding to the information being stored. By heating and subsequent rapid cooling, this charge distribution can be converted into a deformation pattern.

The development by Anderson et al.[2] of thermoplastics which show virtually no aging under thermoplastic[2] and photothermoplastic[7] cycling conditions has solved the problem of poor cycling. For very fast cycling, however, the rate of response of the thermoplastic to heating becomes important. In this stage of the processes, the charge distribution on the thermoplastic surface is converted into a deformation pattern by heating to such a temperature that the electrostatic forces resulting from the remaining surface charge exceed the surface tension of the thermoplastic under conditions of fluidity which allow rapid deformation. This deformation pattern can then be fixed by rapid cooling, or erased by heating

to a higher temperature at which the electrical discharge of the layer has reduced the electrostatic forces below those due to the surface tension, resulting in the regaining of a flat surface.

The rate of response of a thermoplastic is a direct function of the rate of change of its rheological properties with temperature and, in particular, its viscosity. Under recording and erasure conditions, shear forces are small and hence, particularly for low molecular weight polymers, the viscosity under consideration is the Newtonian zero shear viscosity η_0. Kauzmann and Eyring[8] have found that η_0 displays a dependence on the absolute temperature T of the form

$$\eta_0 = A \exp \left(\frac{E_A}{RT}\right) \tag{1}$$

where E_A is the activation energy of flow, A is a constant, and R is the gas constant. The size of E_A, therefore, determines the rate of response of the devices to development and erasure and also the rate of cold flow under storage conditions. Since the rate of response increases with increasing E_A, the optimization of E_A is critical for a device with a rapid response time, e.g., ms range. This paper reports a study of the dependence of E_A on changing composition and changing molecular weight (M_n = 900 to 9000) for a series of methacrylate–styrene copolymers.

EXPERIMENTAL

Preparation

The monomers and initiator used were variously supplied by Ferak, Fluka, and Merck, and, with the exception of styrene, which was vacuum distilled before use, were used without further purification. The copolymers and homopolymers were prepared by polymerizing 0.25 mole monomer mixture or monomer, respectively, dissolved in 100 ml toluene in the presence of between 0.4 and 25 g of α,α'-azobisisobutyronitrile, as initiator, at 67°C under reflux conditions for up to 48 hr. The resulting solution was diluted with 100 ml toluene and then added dropwise to cold methanol (−78°C) with continual stirring. The solid copolymer was recovered by filtration, washed with methanol, and vacuum dried at 80°C for several hours; it was then suitable for use. The yields obtained varied between 10% and 80% and depended strongly on the initiator concentration. Elemental analyses showed that the compositions corresponded, to a good approximation, to the composition of the initial monomer mixture, i.e., within 6.1% and 1.6% for the methacrylate and styrene concentrations, respectively.

The constancy of the copolymer composition with changing chain length can be adjudged from the reactivity ratios (r) reported in the literature.[9] Averaging of the values given by Brandrup et al.[9] for styrene–methyl, ethyl, n-butyl, glycidyl, and isobornyl methacrylate systems yields r_1 and r_2 values of 0.5 ± 0.1 and 0.5 ± 0.1 for styrene–methacrylate and methacrylate–styrene, respectively. In addition, Funt et al.[10] have used ^{14}C-labeled styrene to prepare a methyl methacrylate–styrene copolymer and have found that the specific activities of the GPC-eluted fractions, and hence compositions, were independent of molecular weight. The molecular weight distribution coefficients (M_w/M_n) of 20 representative copolymers were found to be 1.68 ± 0.20. These values are consistent
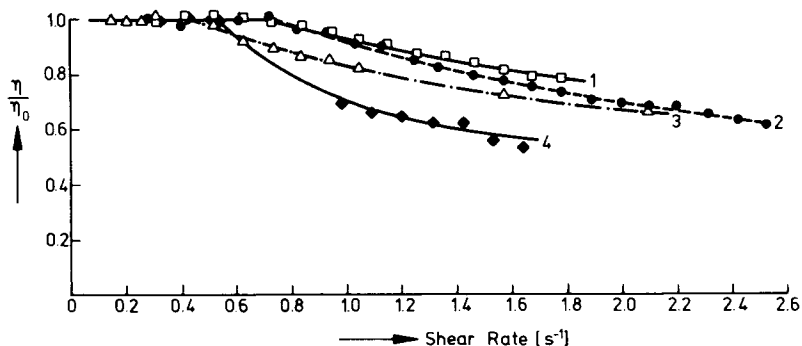
Fig 1. Dependence of relative viscosity (η/η_0) upon shear rate at constant η_0 and molecular weight (M_n = ca. 2670) for methacrylate–styrene copolymers containing: (1, -□-) 15 mole % n-hexyl methacrylate at 140°C; (2, . . . ● . . .) 15 mole % n-dodecyl methacrylate at 150°C; (3, - · - · △ · · -) 15 mole % cyclohexyl methacrylate at 190°C; (4, —♦—) 15 mole % n-tridecyl methacrylate at 130°C.

with those obtained by Anderson et al.[2] for methacrylate–styrene copolymers using a similar preparation technique.

Measurements

The number-average molecular weights (M_n) were determined using a Knauer vapor pressure osmometer, with benzene as the solvent and benzil as the calibrating substance. The calibration was further checked by a narrow molecular weight distribution calibration sample of polystyrene (M_v = 3600) obtained from Ferak. The values of M_n were accurate to within ±5%. The molecular weight distributions were determined using a Waters GPC 200 with tetrahydrofuran as solvent. The relative weight-average (M_w) and number-average (M_n) molecular weights were accurate to 5% and 7%, respectively. The glass transition temperatures T_g were measured with a Perkin–Elmer DSC 1B at a heating rate of 16°C/min. The densities were measured using a mercury displacement pyknometer and were accurate to within 0.5%.

The shear rate program facility of a Haake Rotovisco 3 viscometer, equipped with an oven which enabled plate-cone measurements to be made up to 340°C, was used for the viscosity measurements. The resulting stress–shear rate curves were extrapolated to the shear rate-independent viscosity (i.e., low shear rate Newtonian) region, a minimum shear rate of 1.67×10^{-3} sec^{-1} being obtainable with this apparatus.

RESULTS AND DISCUSSION

Activation Energies of Viscous Flow

In all viscosity measurements, the stress–shear rate curves displayed a shear rate-independent viscosity region as shown, for example, in Figure 1. These zero shear viscosities η_0 were plotted against absolute temperature T in the form of an Arrhenius plot, i.e., ln η_0 versus $1/T$, as shown for several polymers in Figure 2.
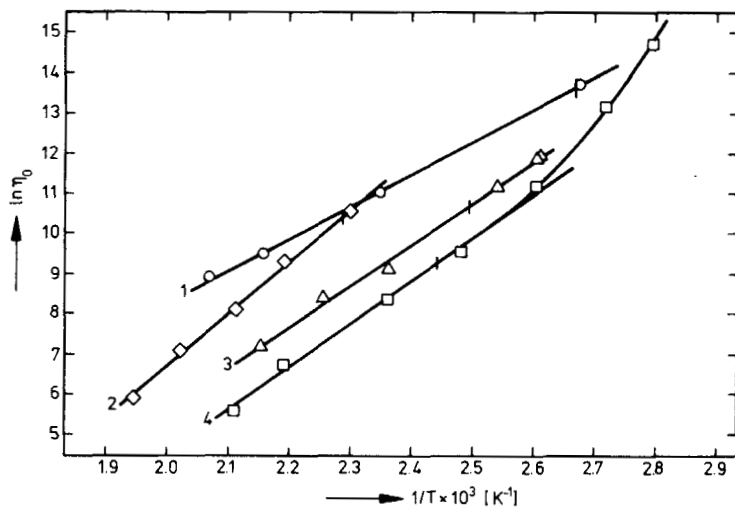
Fig. 2. Dependence of $\ln \eta_0$ on $1/T$ ($^{\circ}K^{-1}$) for polymers containing: (1) 100% styrene (i.e., polystyrene), $M_n = 970$; (2) 25 mole % 2-ethylhexyl methacrylate, $M_n = 9165$; (3) 15 mole % n-dodecyl methacrylate, $M_n = 3450$; (4) 15 mole % 2-ethylhexyl methacrylate, $M_n = 2549$.

It is reported in the literature[11] that linear Arrhenius plots can only be expected in the temperature range above that described by the Williams–Landel–Ferry relationship,[12] i.e., $T_g < T < (T_g + 100)$. In Figure 2, the ($T_g + 100$) temperatures are marked by vertical lines in each case. Line 4 shows the expected deviation from linearity at temperatures below ($T_g + 100$). The compositions, M_n values, and T_g values of the polymers shown in this figure are given in Table I.
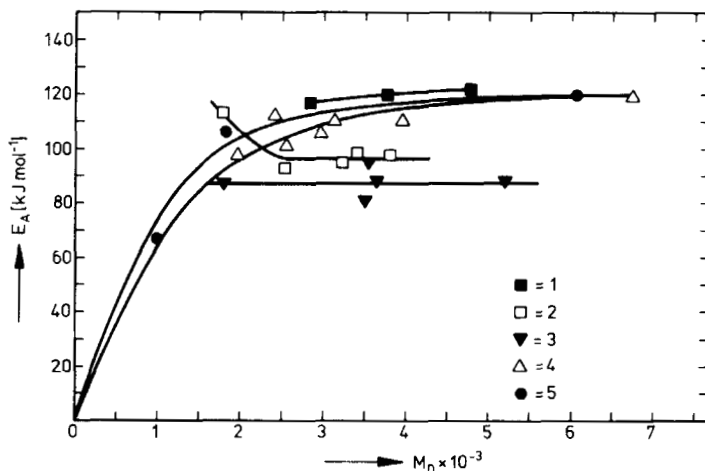

Fig. 3. Dependence of activation energy E_A of viscous flow on M_n for copolymers containing: (1, ■) 10.7 mole % n-octyl methacrylate; (2, □) 15 mole % 2-ethylhexyl methacrylate; (3, ▼) 20 mole % n-decyl methacrylate; (4, △) 15 mole % cyclohexyl methacrylate; (5, ●) polystyrene.

The activation energies E_A of viscous flow obtained from the Arrhenius plots have been plotted against molecular weight (M_n) for polystyrene (line 5) and

several of the methacrylate–styrene copolymer compositions investigated (lines 1–4) in Figure 3. It can be seen that above a certain molecular weight, E_A tended toward as asymptotic limit whose exact value could not be established in the absence of higher molecular weight copolymers. This is consistent with the observation by Fox et al.[14] that with increasing molecular weight, E_A tended toward an asymptotic limit at a molecular weight of 15,000 for homopolymers, as does T_g. The highest quasi-asymptotic values of E_A for copolymers, i.e., for those containing 10.7 mole % n-octyl methacrylate (line 1) and 15 mole % cyclohexyl methacrylate (line 4), approached that of polystyrene (line 5). The E_A values of the latter were consistent with those reported in the literature.[15–18] For several copolymer compositions, a decrease in E_A with increasing molecular weight was observed at molecular weights below that at which a molecular weight-independent value was observed, e.g., for copolymers containing 15 mole % 2-ethylhexyl methacrylate (see Fig. 3, line 2). No satisfactory explanation has been found for this phenomenon.

TABLE I

Compositions, M_n Values, and T_g Values for Samples of Polystyrene and Several Methacrylate–Styrene Copolymers

Line no.	Methacrylate type	Methacrylate, mole %	Styrene, mole %	M_n	T_g, °K
1	—	—	100	970	270[a]
2	2-Ethylhexyl	25	75	9165	336
3	n-Dodecyl	15	85	3450	301
4	2-Ethylhexyl	15	85	2549	310

[a] Calculated from relationship in ref. 13.

In Figure 4, E_A is plotted against mole % methacrylate in the copolymer for a series of methacrylate–styrene copolymers, containing n-octyl, n-heptyl, cyclohexyl, n-decyl, and n-dodecyl methacrylate, with approximately constant molecular weight. With the exception of n-octyl methacrylate–styrene copolymers (line 1), the E_A values correspond to the molecular weight-independent regions indicated in Figure 3. These molecular weight-independent E_A values increase, e.g., cyclohexyl methacrylate–styrene copolymers (line 3); are approximately constant, e.g., n-heptyl methacrylate–styrene copolymers (line 2); or decrease, e.g., n-decyl and n-dodecyl methacrylate–styrene copolymers (lines 4 and 5), in a continuous manner with increasing methacrylate concentration. In the case of n-octyl methacrylate–styrene copolymers (line 1), a sharp maximum was observed at about 5 mole % n-octyl methacrylate.

In addition to the variation in the form of the E_A–methacrylate concentration dependences with the methacrylate concerned, it can also be seen from Figure 4 that the values of E_A observed at the same methacrylate concentration were also strongly dependent on the methacrylate present. This variation is highlighted in Figure 5a, b, and c by the maxima obtained when the molecular weight-independent values of E_A were plotted against the number of carbon atoms in the methacrylate straight-chain ester group for copolymers containing 10, 15, and 20 mole % methacrylate, respectively. Wang et al.[19] have observed a similar effect with a poly-1-olefin series in which a sharp maximum was observed in the dependence of E_A on monomer molecular weight in the composition
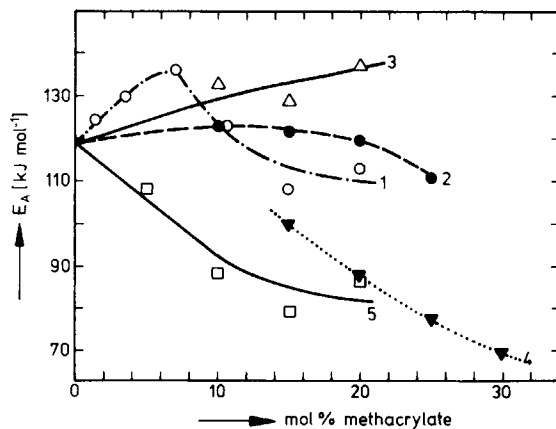
Fig. 4. Dependence of E_A (kJ/mole) on mole % methacrylate in the copolymer for: (1, - - -○- - -) n-octyl methacrylate–styrene copolymers, M_n = ca. 2530; (2, - - -●- - -) n-heptyl methacrylate–styrene copolymers, M_n = ca. 3510; (3, —△—) cyclohexyl methacrylate–styrene copolymers, M_n = ca. 3950; (4, ··· ▼ ···) n-decyl methacrylate–styrene copolymers, M_n = ca. 3510; (5, —□—) n-dodecyl methacrylate–styrene copolymers, M_n = ca. 3660.

range from poly-1-hexene to poly-1-octene. An explanation of these maxima can be obtained by examining the quantities involved. The activation energy E_A of viscous flow for long-chain molecules has been interpreted by Kauzmann and Eyring[8] as being that energy required to create a hole for the kinetic chain unit (i.e., that chain segment which moves as a unit under the influence of shear) to move into and hence exp (E_A/RT), see eq. (1), is the probability that a sufficiently large hole will be available. The size of the required hole will be a function of the volume of the kinetic chain length, which is temperature independent, and the availability of free volume, which will be a function of temperature and the expansion coefficient α. Comparison of eq. (1) with that from Doolittle's[20] free-volume theory, as interpreted by Williams,[21] i.e.,

$$\eta_0 = A e^{B/f} \qquad (2)$$

where f is the relative free volume and is $[f_g + \alpha(T\text{-}T_g)]$ at temperatures above the glass transition temperature T_g and $\alpha'T$ at temperatures below T_g; $f = (v - v_0)/v_0$; and f_g, the relative free volume at T_g, is given by $(v_g - v_0)/v_0$, where v is the specific volume, v_0 is the zero volume, and v_g is the specific volume at T_g; and B is a constant; shows that E_A is a function of α. Thus, assuming that similar polymers of comparable chain length have comparable kinetic chain lengths, E_A will depend on the bulk of the chain substituents and on the expansion coefficient α, which is related to the specific volume as was shown above. Figure 5a, b, and c, however, show E_A as a function of the number of carbon atoms in the methacrylate straight-chain ester group at approximately constant chain length and hence as a function of the bulk of the methacrylate ester groups. Such dependences will, however, conceal any changes in the bulk density (= $1/v$) of the copolymers due to a change in the bulk of the methacrylate ester groups.

This possibility is explored in Figure 6 in which the dependences of E_A and density upon the number of carbon atoms in the straight-chain ester methacrylate are compared for methacrylate–styrene copolymers of similar molecular weight containing 15 mole % methacrylate. It is evident that no maximum was
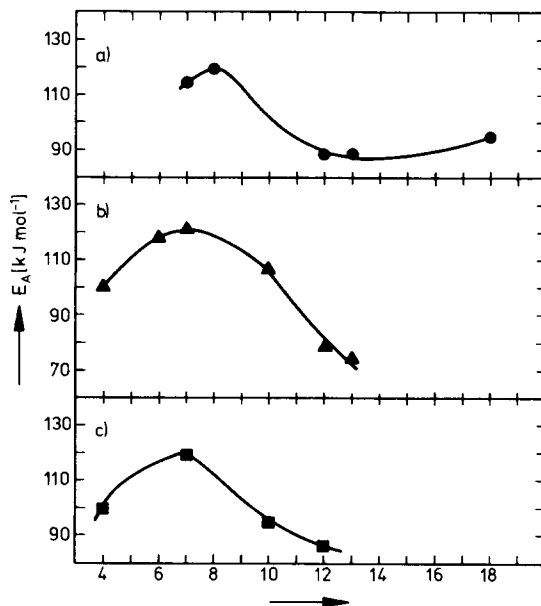
Fig. 5. Dependence of E_A (kJ/mole) on number of carbon atoms in the methacrylate straight-chain ester group for copolymers containing: (a) 10 mole % methacrylate, M_n = ca. 3720; (b) 15 mole % methacrylate, M_n = ca. 3650; (c) 20 mole % methacrylate, M_n = ca. 3800.

observed in the density dependence and hence that, at least for straight-chain methacrylate esters with less than seven carbon atoms in the ester group (i.e., n-butyl and n-hexyl methacrylate), the density was not the controlling factor in the form of the E_A dependence.   Thus, it must be concluded that the bulk of the methacrylate ester groups is the controlling factor for copolymers containing straight-chain methacrylate esters with less than seven carbon atoms in the ester group.

Let us now examine the dependence of E_A on the substituent molar volume per monomer unit, as this enables the dependences shown in Figure 5a, b, and c to be examined in the context of other polymers.   Schott[15] has reported a correlation between the substituent molar volume per monomer unit, calculated using the elemental volume equivalents of Le Bas[22] for a vinylidene monomer unit ($CH_2{=}CR_1R_2$), and E_A for several polyolefins and polystyrene.   Porter et al.[11] have extended his data to include poly(vinyl acetate) and other polymers.

Figure 7 shows a similar plot including more recent literature data for homopolymers[19,23–25,27] and our data for copolymers containing 15 mole % methacrylate (continuous line) and 20 mole-% methacrylate (broken line).   It can be seen that at low substituent molar volumes, E_A tends to increase with increasing molar volume up to a maximum of between 90 and 160 ml (Le Bas units) and then decreases.   Those polymers for which ranges are given exhibit either a dependence of E_A on molecular weight distribution [(polyethylene and poly(methyl methacrylate)],[23] or stereoregularity (polypropylene),[24] corresponding to the ranges given; and hence, only averaged values can be compared with the other values.   The data for copolymers containing 15 and 20 mole % methacrylate were
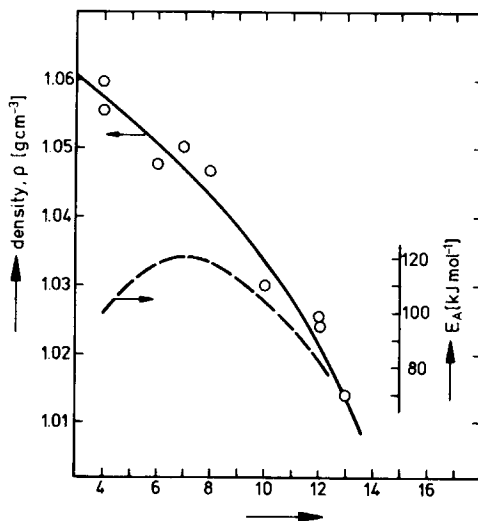
Fig. 6. Dependences of density ρ (g/cm^3) at 20°C and E_A (kJ/mole) on number of carbon atoms in the methacrylate straight-chain ester group for copolymers containing 15 mole % methacrylate.

largely confined to molar volumes between 110 and 160 ml; and hence, the maxima found with these data coincide approximately with that for the literature data and in particular that for poly-1-olefins[19] (open circles). The decrease in E_A with increasing substituent molar volume after the maxima was paralleled, both for the copolymers and for the polymethacrylates[27] (inverted triangles), by a decrease in density and hence an increase in the available free volume. It would, therefore, seem reasonable to propose that a critical substituent molar volume exists below which E_A increases with substituent volume, due to the increasing substituent bulk being the determining factor, and above which E_A decreases with substituent volume, due to the decreasing density being the determining factor.

The implication of this critical molar substituent volume for the production of thermoplastic layers with optimal response rates is that only methacrylate–styrene copolymers with a molar substituent volume in the region of the critical value, i.e., 96–140 ml (Le Bas units), will have sufficiently high activation energies of flow to ensure an optimal η_0–temperature dependence. Further, assuming a substituent molar volume in this range, it can be seen from Figures 4 and 5 that copolymers containing up to 15 mole % n-heptyl, 15 mole % n-octyl, or 20 mole % cyclohexyl methacrylate will exhibit optimal E_A values and, in particular, if M_n values are chosen corresponding to the maximum in the E_A–M_n characteristic. A secondary consideration in the selection of an approprite thermoplastic is the temperature at which development and erasure take place. This should be sufficiently low to allow development and erasure with the minimum amount of heat energy, without unduly increasing the rate of cold flow at the storage temperature. Such criteria were satisfied by (n-heptyl and n-octyl methacrylate–styrene) copolymers containing up to 15 mole % methacrylate.
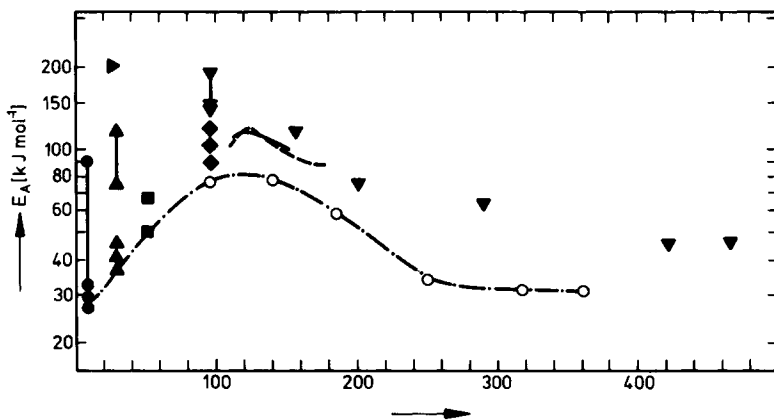
Fig. 7. Dependence of E_A (kJ/mole) on substituent molar volume per chain unit in ml (Le Bas units [22]): (●) polyethylene;[15,23] (▲) polypropylene;[15,24] (▶) poly(vinyl chloride);[25] (■) poly(vinyl acetate);[15] (◆) polystyrene;[15,26] (▼) poly(methyl methacrylate)[15] and polymethacrylates (methyl, n-butyl, n-hexyl, n-decyl, n-hexadecyl, and n-octadecyl);[27] (- · O - ·) poly-1-olefins (polyethylene, polypropylene, poly-1-butene, poly-1-hexene, poly-1-octene, poly-1-decene, poly-1-tridecene, poly-1-hexadecene, poly-1-octadecene).[19]

Critical Molecular Weights

The data discussed above were primarily obtained to yield information on the activation energy E_A of viscous flow. However, very few data on the zero shear viscosities of copolymers have been published,[28] and hence it is of interest to examine the η_0–M_w dependences of several of the copolymer compositions investigated. Care was taken to obtain η_0 data at sufficiently high temperatures to enable the theoretical linear dependence of η_0 on M_w, in the absence of intermolecular entanglement, to be observed.[28] The η_0–M_w dependences obtained are shown in Figure 8. Lines 1, 2, and 3, corresponding to copolymers containing 5 and 10 mole % n-dodecyl methacrylate and 20 mole % n-decyl methacrylate, respectively, clearly show a η_0–M_w dependence which approximates a 3.4 power, whereas lines 5 and 6, corresponding to copolymers containing 10.7 mole % n-octyl methacrylate and 15 mole % cyclohexyl methacrylate, show a η_0–M_w dependence which is approximately linear. Line 4, corresponding to copolymers containing 15 mole % 2-ethylhexyl methacrylate, may show a transition between the former and latter types of dependence.

In general, an abrupt increase in the power dependence of η_0 upon M_w from ca. 1 to ca. 3.4 has been taken to indicate the transition of polymer chains in a free state to a state of intermolecular entanglement.[28,29] It would, therefore, appear that lines 5 and 6 represent a nonentangled situation and that the molecular weights corresponding to the transition to entanglement M_c lie at molecular weights greater than 8000 and 12,000, respectively. This is entirely consistent with the observation of M_c values of 31,200 and 27,500 for polystyrene and poly(methyl methacrylate), respectively.[28] However, lines 1, 2, 3, and 4 indicate entanglement at molecular weights down to below 2500, 2700, and 3200; and to 5630, respectively. Available literature data on copolymeric systems,[28,30] however, have indicated very low critical chain length values Z_c. Solution data on acrylonitrile–methyl methacrylate copolymers containing 90% acrylonitrile

have yielded[30] a Z_c value of 50; and melt data on ethylene–propylene copolymers with 16%, 56%, and 70% ethylene have yielded, Z_c values of 31, 56 and 43.[28] These were consistent with the Z_c values obtained for copolymers containing 5 mole % and 10 mole % n-dodecyl, 20 mole % n-decyl, and 15 mole % 2-ethylhexyl methacrylate, i.e., <45, <45, <43, and 95, respectively. These values, together with those for copolymers containing 10.7 mole % n-octyl methacrylate and 15 mole % cyclohexyl methacrylate, are summarized in Table II.
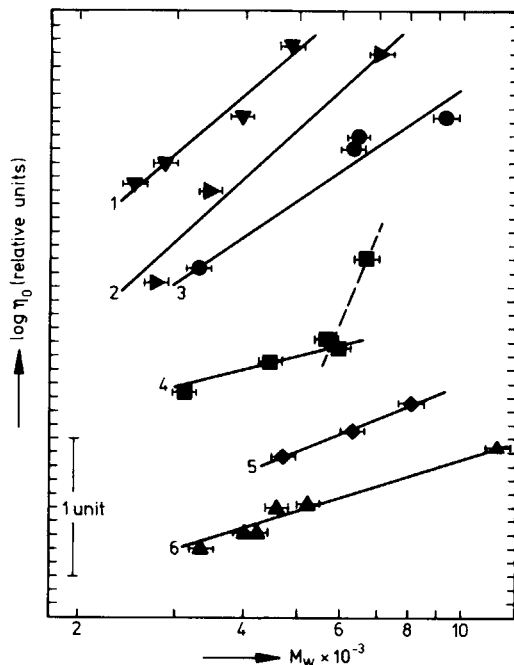

Fig. 8. Dependence of log η_0 on M_w for copolymers containing: (1) 5 mole % n-dodecyl methacrylate; (2) 10 mole % n-dodecyl methacrylate; (3) 20 mole % n-decyl methacrylate; (4) 15 mole % 2-ethylhexyl methacrylate; (5) 10.7 mole % n-octyl methacrylate; (6) 15 mole % cyclohexyl methacrylate.

Thus, the data can be divided into two groups—those showing affinity to homopolymers and copolymers, respectively. The observation of a high M_c value for methacrylate–styrene copolymers containing 15 mole % cyclohexyl methacrylate can be explained by the chain stiffening effect of the bulky cyclohexyl group as suggested by Porter et al.[30] The remaining data can be explained by a decrease in M_c with increasing methacrylate ester chain length and increasing methacrylate concentration.

CONCLUSIONS

The activation energies E_A of viscous flow of methacrylate–styrene copolymers (M_n = 900–9000; M_w/M_n = 1.68 ± 0.20) have been found to exhibit a strong dependence on composition, methacrylate monomer, and molecular weight (at low molecular weights). Such behavior has been explained in terms of an increase in E_A with the molar volume of the pendent substituents up to a critical

TABLE II
Compositions, Critical Molecular Weights M_c, and Chain Lengths Z_c for Several
Methacrylate–Styrene Copolymer Compositions

Line no.	Methacrylate type	Methacrylate, mole-%	Styrene, mole-%	M_c	Z_c
1	n-Dodecyl	5	95	<2500	<45
2	n-Dodecyl	10	90	<2700	<45
3	n-Decyl	20	80	<3200	<43
4	2-Ethylhexyl	15	85	5630	95
5	n-Octyl	10.7	89.3	>8000	>140
6	Cyclohexyl	15	85	>12000	>211

molar volume (120 ± 10 ml Le Bas units) and a decrease in E_A with increasing substituent molar volume above this value due to the decreasing density of the copolymer.

Copolymers with substituent molar volumes in the range of 96 to 140 ml had viscosity–temperature characteristics that made them suitable for application in photothermoplastic and thermoplastic devices in which the development and erasure processes could be carried out rapidly with a relatively low expenditure of heat energy.

Methacrylate–styrene copolymers containing long-chain ester methacrylates (viz., n-decyl and n-dodecyl methacrylate) have been shown to exhibit very low critical molecular weights and chain lengths, indicating intermolecular entanglement at very low molecular weights. The critical molecular weights and chain lengths were found to decrease with increasing methacrylate ester chain length and increasing methacrylate concentration.

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