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Influence of molar mass on the diffusion and solubility behaviour of methyl ethyl ketone–isopropyl alcohol mixtures in poly(methyl methacrylate)

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Poly(methyl methacrylate) PMMA is used extensively as an electron beam resist. The development of the lithographic pattern after exposure of the polymer to electron beam irradiation is achieved by contacting the film with a solvent mixture of isopropyl alcohol and methyl ethyl ketone. In this paper the mutual diffusion coefficients for isopropyl alcohol–methyl ethyl ketone mixed solvents into PMMA of narrow molar mass distribution with a range from 49000 to 400000 g mol^{-1} are reported. The mutual diffusion coefficient indicates that the behaviour was both a function of molar mass and solvent composition. The ability for the PMMA to swell in the solvent was found to be molar mass dependent. Cloud point measurements on solutions indicated that change in the molar mass influenced the temperature at which precipitation occurred in the mixed solvents. The cloud points also depended on the quality of the solvent; occurring at lower temperature for the better solvent [1 : 1 w/w isopropyl alcohol (IPA)–methyl ethyl ketone (MEK)] and being higher for the poorer solvent (4 : 1 w/w IPA–MEK). The swelling characteristics indicate that an increase in the degree of chain entanglement leads to suppression of the degree of swelling. The electron beam sensitivity suggests a complex interplay of the effects of the molar mass on the chain scission process, on the ability of solvent to enter the degraded matrix and on the solubility of the polymer on the solvent mixture. The casting solvent has an effect on the structure of the solid and influences the behaviour of the films when exposed to the developing solvent.

Introduction

Many electron beam resists are based on PMMA and the development of the lithographic pattern is achieved by the use of mixtures of isopropyl alcohol (IPA) and methyl ethyl ketone (MEK). In a previous paper[1] the effects of change of composition of mixtures of IPA and MEK on the mutual diffusion coefficients for poly(methyl methacrylate) (PMMA) were investigated. The diffusion of the solvent mixture into the polymer film is selective and preferential for methyl ethyl ketone. The mutual diffusion coefficient decreases and becomes asymmetric towards low values of the solvent mixture as the proportion of isopropyl alcohol is increased. The higher glass transition temperature films are prone to crazing and this influences the overall development process. The diffusion of the solvent mixture into PMMA is complex and involves a lowering of the glass transition temperature, precipitation of the polymer by the non-solvent—isopropyl alcohol—and polymer dissolution. Electron beam lithography is based on radiation-induced degradation of the polymer producing regions of lower molar mass materials. The development of the pattern involves the selective removal of these areas of lower mass material without significantly modifying the unexposed areas. The mechanism of dissolution of PMMA is very different from that appropriate for photoresis material.[2]

Isopropyl alcohol is a non-solvent for PMMA, whereas MEK is a good solvent for PMMA.

Changes in the solvent mixture and in the temperature used for the development process result in the mixture changing from being a good solvent to becoming a poor solvent for the polymer.[3] Since solubility is a function of molar mass, it is possible to select a mixture which will selectively dissolve the low molar mass material without significantly swelling the unexposed higher molar mass components.[4,5]

In this paper, the results of a study of the effects of solvent variation on the dissolution process for narrow molar mass distribution PMMA, having a range of molar masses lying between 49000 and 400000 g mol^{-1} are examined. The range of molar masses was selected to simulate the differences in molar mass which will be generated during the electron beam degradation process.

Experimental

Materials

Poly(methyl methacrylate) was obtained from Polymer Laboratories plc, Shrewsbury, UK. The samples of PMMA had molar mass distributions between 1.10 to 1.06 and molar masses of 49000, 79000, 127000, 265000 and 400000 g mol^{-1}. Methyl ethyl ketone and isopropyl alcohol were used as solvents, obtained from Merck (Poole, UK) as AnalaR grade reagents. The films used were produced by spinning a 3 wt% solution of PMMA in MEK onto a chromium-coated glass substrate, using a Headway Research Incorporated spinner, operating with speeds between 1000 and 500 revolutions per minute.[6] The spun films were baked at 130 °C for 1 h, before being used in these studies.

Fabry Perot interferometer experiment

The interferometer construction and its operation have been described in a previous paper.[6] The traces were used to calculate the concentration–distance curves from which the mutual diffusion coefficients were calculated.

Data analysis

In the analysis, it was assumed that the refractive index is linearly proportional to concentration and that there is negligible volume change on mixing of polymer and solvent. The profiles were recorded at 3 min intervals and the fringe traced from the photographic representation.

Measurement of the cloud points for the polymer solutions

The cloud points were determined by placing 0.2 cm^3 of polymer solution into a capped glass tube having 3 mm thick glass walls, a 3 mm internal diameter and 15 cm length. The sample was then immersed in a water bath and heated until the solution became clear. After equilibration for 1 h, the tube was then slowly cooled at a rate of 0.1 °C min^{-1} until the solution became cloudy. The temperature of the solution was observed using a resistance thermometer, attached intimately to the outside of the tube. The values quoted are the mean of four measurements and the average spread in the temperatures was less than ± 1 °C.

Electron beam characterisation of the PMMA films

PMMA films, with a thickness of approximately 1 μm and an area 1.25 × 1.25 cm, were deposited on chromium-coated glass cover slips and baked for 1 h at 130 °C. Electron beam exposure was carried out in a modified Philips electron microscope which allowed scanning of the film using a computer-controlled raster drive. A pattern consisting of a series of boxes, with the doses ranging between 1×10^{-4} and 1×10^{-3} C cm^{-2}, in 36 steps and having dimensions of 57 × 32 μm, was produced. A second pattern using dose rates between 1×10^{-5} to 1×10^{-4} C cm^{-2}, in 35 steps and using boxes of size 192 × 108 μm was also used. Each experiment was repeated at least three times. The films were developed using a 7:3 w/w IPA–MEK mixture for periods of time ranging from 45 to 180 s. The developed films were baked at 100 °C for 30 min before measurement of the dissolution rates assessed from step sizes, obtained using a Dektac surface profile analyser.

Results and discussion

Mutual diffusion coefficient measurements

The diffusion behaviour is discussed in terms of three solvent compositions: 1:1 w/w IPA–MEK, 3:2 w/w IPA–MEK and 7:3 w/w IPA–MEK. These compositions span those typically used for the development of electron beam resists.

1:1 w/w IPA–MEK

It was observed in a previous paper[1] that this mixture is a good solvent system for PMMA. This is also true of all the molar masses studied in this paper (Fig. 1). However, there are significant differences between the lower molar mass PMMA polymers (49000 and 79000 g mol^{-1}) and the higher molar mass materials. The observation of two peaks, in the mutual diffusion coefficient *versus* composition profile, indicates very rapid diffusion of the polymer molecules into the solvent and solvent molecules into polymer. These processes are slowed down considerably when the molar mass value of PMMA is above 127000 g mol^{-1}. However, in the case of the 400000 g mol^{-1} PMMA, an apparently anomalous higher value of D_m is observed. This may be attributed to the effects of chain entanglement, suppressing densification during the spin casting process. The maximum value of the mutual diffusion coefficients, D_m and their location on the composition axis are summarised in Table 1. Entanglement influences the film forming process and also the swelling and diffusion of solvent during the development process.

3:2 w/w IPA–MEK

With this poorer solvent, a characteristic peaking of D_m at low ϕ_s is observed, reflecting the relative importance of dissolution over solvent penetration in the diffusion process (Fig. 2). The magnitude of the peak decreases with molar mass (Table 1). Above the 127000 g mol^{-1} molar mass value for PMMA, there is a marked decrease in the magnitude of D_m. The absolute

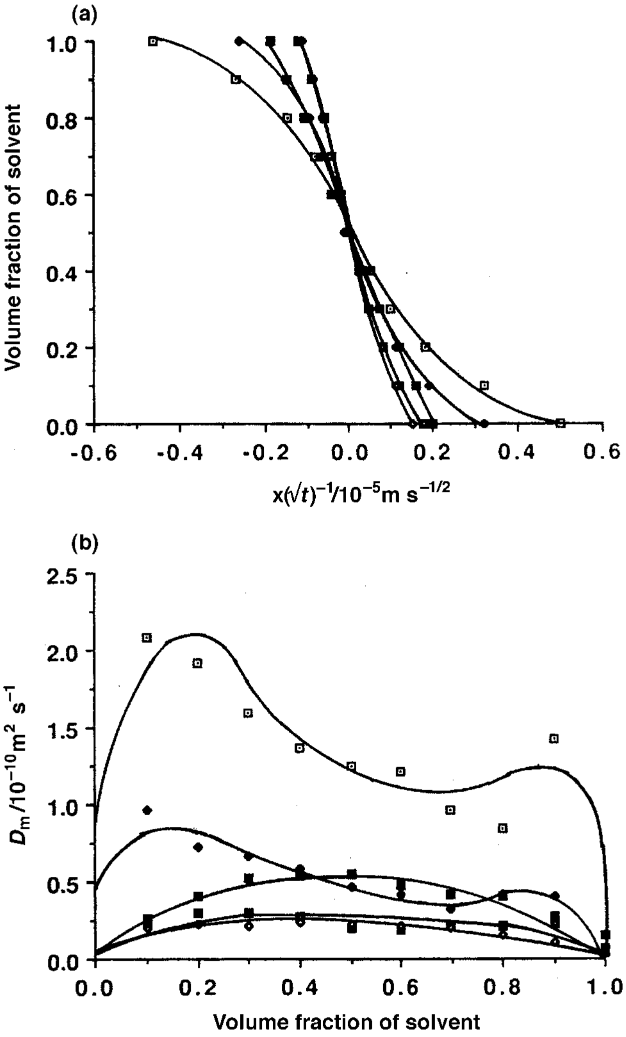

Fig. 1 Boltzmann transformation curves. (a) Volume fraction of solvent *versus* distance/$\sqrt{}$time for 1:1 w/w IPA–MEK. (b) Mutual diffusion coefficients for different solvent mixtures for film A. (⊡) 49000, (◆) 79000, (□) 127000, (◇) 265000 and (■) 400000 g mol^{-1}, respectively. The errors are estimated to be ± 0.05 in the volume fraction in (a) and $\pm 0.01 \times 10^{-10}$ m^2 s^{-1} for each data point in D_m in (b). The errors are greater at the extremes of the compositional variations.

Table 1 Summary of D_m and ϕ_s as a function of molar mass and solvent composition

Solvent composition	Molar mass/ g mol^{-1}	$D_m/10^{-10}$ m^2 s^{-1}	ϕ_s
1:1 w/w IPA–MEK	49000	2.08	0.1
	79000	0.97	0.1
	127000	0.32	0.25
	265000	0.23	0.3
	400000	0.50	0.5
3:2 w/w IPA–MEK	49000	0.21	0.2
	79000	0.18	0.2
	127000	0.12	0.5
	265000	0.16	0.5
	400000	0.16	0.2
7:3 w/w IPA–MEK	49000	0.16	0.2
	79000	0.10	0.15
	127000	0.03	0.1
	265000	0.09	0.15
	400000	0.06	0.2

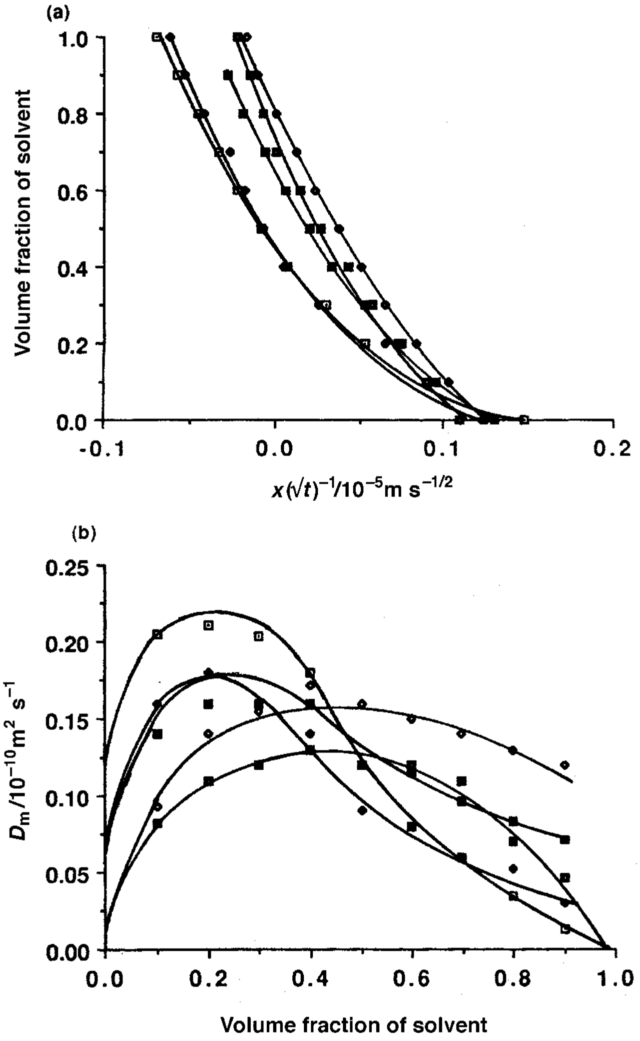

Fig. 2 Boltzmann transformation curves. (a) Volume fraction of solvent *versus* distance/$\sqrt{}$time for 3:2 w/w IPA–MEK. (b) Mutual diffusion coefficients for different solvent mixtures for film A. (⊡) 49000, (◆) 79000, (□) 127000, (◇) 265000 and (■) 400000 g mol^{-1} respectively. The errors are estimated to be ±0.05 in the volume fraction in (a) and $\pm 0.01 \times 10^{-10}$ m^2 s^{-1} for each data point in D_m in (b).

magnitude of D_m is significantly lower than it is for the better solvent system, indicating a slowing down of the permeation process.

7:3 w/w IPA–MEK

In this much poorer solvent (Fig. 3), peaking at low ϕ_s is once more observed. There is also a marked decrease in the diffusion coefficients on increasing the molar mass. The non-monotonic decrease in D_m is an indication of the effects of entanglement on the diffusion process.

Swelling behaviour

The development process is a combination of dissolution and swelling of the polymer matrix. The swelling rate can be directly measured from the movement of the solvent polymer interface during the exposure process. The swelling rate with the lower molar mass polymers in the better solvents (1:1 and 3:2 w/w IPA–MEK) are difficult to measure as the boundary disappears almost immediately the experiment is started. It is only in the poorer solvent system and for the higher molar mass materials that a swelling rate becomes measurable (Fig. 4). The rate of swelling for the solvent mixture 7:3 w/w IPA–MEK decreases from 49000 to 79000 g mol^{-1} molecular mass PMMA. The swelling data for the remaining systems are all within experimental error.

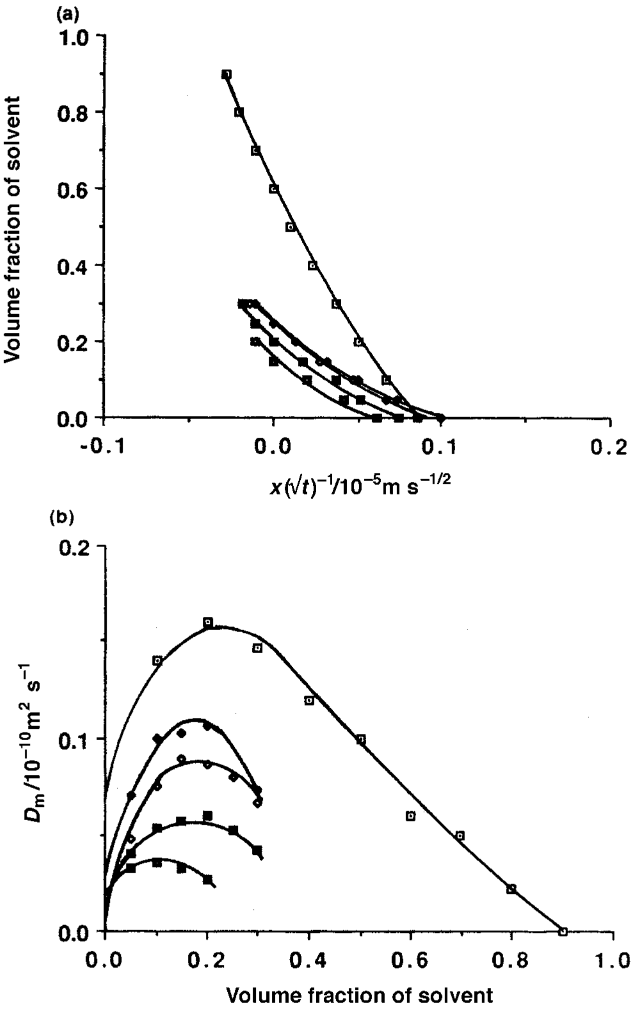

Fig. 3 Boltzmann transformation curves. (a) Volume fraction of solvent *versus* distance/$\sqrt{}$time for 7:3 w/w IPA–MEK. (b) Mutual diffusion coefficients for different solvent mixtures for film A. (⊡) 49000, (◆) 79000, (□) 127000, (◇) 265000 and (■) 400000 g mol^{-1} respectively. The errors are estimated to be ±0.05 in the volume fraction in (a) and $\pm 0.02 \times 10^{-10}$ m^2 s^{-1} for each data point in D_m in (b).

Thermodynamic effects on the dissolution behaviour

Solubility is one of the factors in the dissolution process and can be quantified in terms of the thermodynamic interaction parameter which influences the temperature at which precipitation of the polymer occurs.[7] For polymer solutions, there exist an upper critical solution temperature and a lower critical solution temperature which are a function of the nature of the interaction between polymer and solvent. Changing the solvent composition will change the nature of the solvent–polymer interaction parameter and, hence, the cloud point temperature (Fig. 5). The concentration of the polymer solution (0.6 wt% of polymer in MEK) used in this study corresponds to the dilute solution region and the effects of variation of the molar mass of the polymer used were investigated. There is a very marked molar mass effect and a solvent effect on the cloud point. For the better solvent (1:1 w/w IPA–MEK) all the different molar mass samples are soluble in the mixture at ambient temperature. At 310 K, as the quality of the solvent is decreased, the polymer ceases to be soluble in the solvent. A room temperature development system would use the

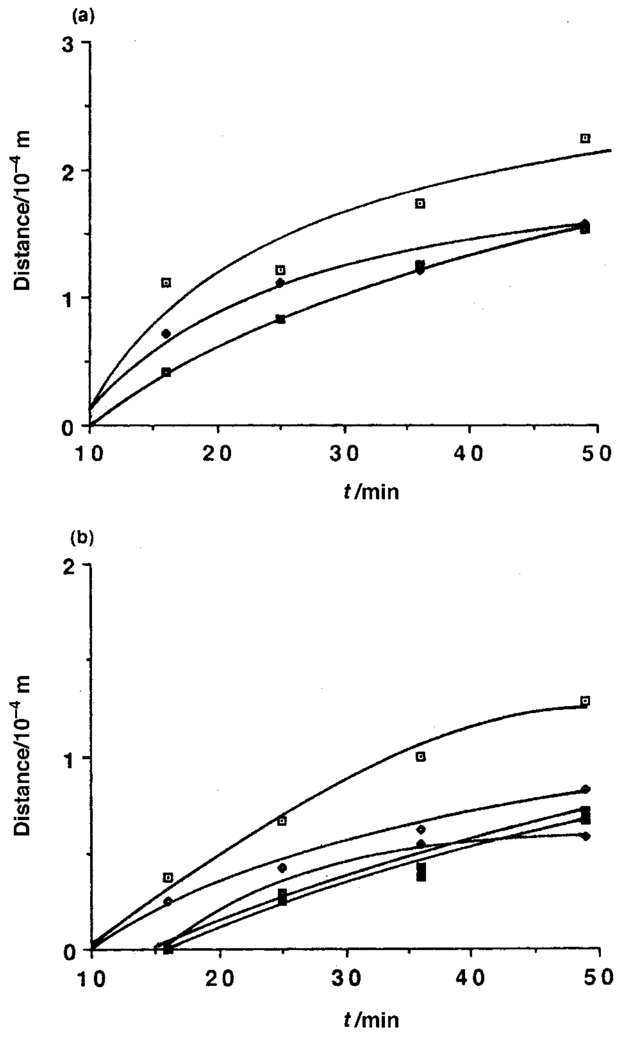

Fig. 4 Swelling rate curves for (a) 3:2 and (b) 7:3 w/w IPA–MEK. (⊡) 49000, (◆) 79000, (□) 127000, (◇) 265000 and (■) 400000 g mol^{-1} respectively. The definition of the distance is determined by the width of the boundary and is on average $\pm 0.1 \times 10^{-4}$ m.

selective solubility to dissolve the lower molar mass polymer whilst not dissolving the higher molar mass material.

Electron beam sensitivity curves

The effect of molar mass on the sensitivity of thin films of PMMA to electron beam irradiation is shown in Fig. 6. The more sensitive the film to electron beam irradiation the lower the dose at which the film is observed to be reduced to half its usual thickness, usually designated D_{50}. Values for D_{50} are presented in Table 2. The films obtained from 265000 and 12700 g mol^{-1} samples of PMMA exhibit the greatest sensitivity to electron beam irradiation. The films obtained from the lower molar mass samples (27000 and 49000 g mol^{-1} PMMA) are less easily degraded. The films obtained from the highest molar mass material (400000 g mol^{-1} PMMA) require the highest electron beam dose for the generation of the pattern. The electron beam exposure produces chain scission and lowers the average molar mass of the polymer. It would, therefore, be expected that, since solubility is a function of the molar mass, the sensitivity should correlate with the molar mass of the original films. However, in practice, degradation of a high molar mass material could generate mass fractions which are still sufficiently high to allow entanglement even in the irradiated film. Hence, the response of the films to the

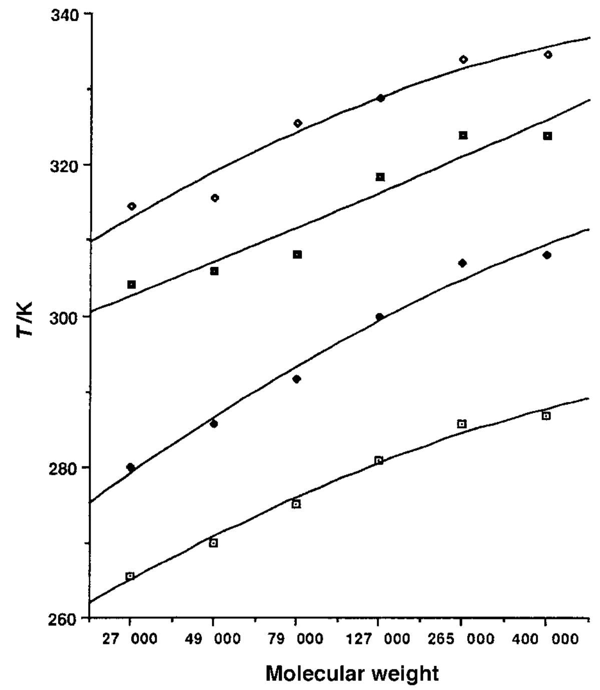

Fig. 5 Cloud point temperature *versus* molar mass for PMMA and various compositions of IPA–MEK. (⊡) 1:1, (◆) 3:2, (■) 7:3 and (◇) 4:1 w/w IPA–MEK.

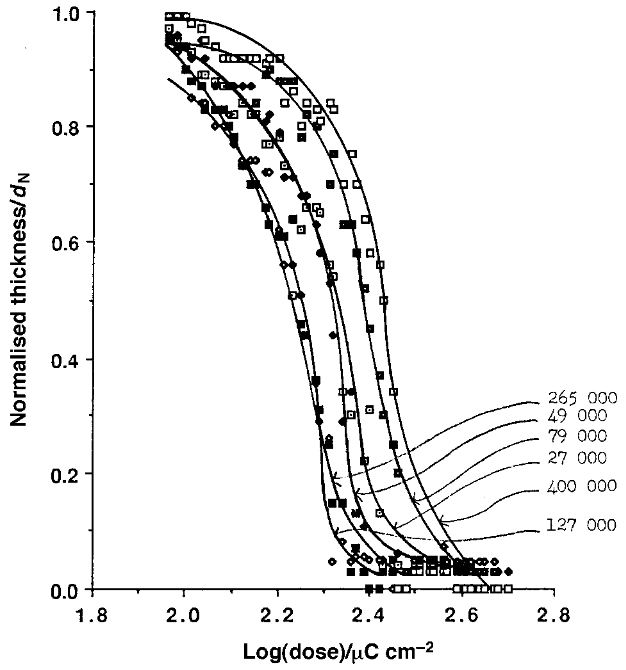

Fig. 6 Electron beam sensitivity curves for narrow molar mass PMMA. (⊡) 27000, (◆) 49000, (□) 79000, (◇) 127000, (■) 265000 and (□) 400000 g mol^{-1} respectively.

Table 2 Values of D_{50} for PMMA of different molar mass

Polymer	Molar mass	D_{50}/μC cm^{-2}
PMMA	27000	2.315
	49000	2.240
	79000	2.390
	127000	2.230
	265000	2.220
	400000	2.410

developer would be influenced by entanglement effects. The sensitivity will therefore a function of:

(i) The structure of the polymer in the spin cast films. This is a well-known effect and indicates the influence of both the casting solvent and the T_g of the final film, dictated by the pre-exposure, baking procedures.

(ii) The solvent, time and temperature used in the development process. With the solvent system and temperature held constant, the time for development was varied so as to achieve the optimum conditions for polymer removal. The exposure time was varied between 45 and 90 s. The most sensitive films required a slightly longer exposure to developing solvent than was needed by the lower molar mass materials. Once more, the effects of the frozen-in, non-equilibrium conformation may be playing a role in terms of defining the final ranking of the sensitivity of the polymers. From our previous studies,[8] we know that in the case of the 265000 and 129000 g mol^{-1} molar mass PMMA materials, irradiation with the electron beam would have generated material with molar masses in the range 40000–60000 g mol^{-1} which will be very soluble and hence easily removed. Irradiation of the lower molar mass PMMA material could generate material with molar masses in the range 20000–30000 g mol^{-1} which, in principle, should be more easily removed. However, having a lower degree of entanglement could generate on spinning a more dense solid which will be less easy to remove than the more expanded, higher molecular weight material. The sensitivity is therefore not only a function of the dissolution characteristics of the regions formed on exposure, but is also controlled by the spinning and baking processes, prior to exposure. These findings are in agreement with experimental observations.[8–12]

Conclusions

The effects of the change of molar mass on the mutual diffusion coefficient, solubility and electron beam sensitivity are reported for a series of different molar mass and different solvent systems. The observed changes can be rationalised in terms of accepted theory of random choice scission and the effects of molar mass on the solubility of the degraded polymer elements and their interaction with the polymer matrix. However, there are anomalies which reflect the frozen-in conformational constraints on formation of the solid films.

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