

Synthesis and Characterization of a Poly(methyl methacrylate–acrylic acid) Copolymer for Bioimplant Applications

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SYNOPSIS

This paper describes the development of a new crosslinked poly(methyl methacrylate–acrylic acid) copolymer for potential applications in bone implants. This copolymer, comprising hydrophobic and hydrophilic components, has been designed to provide small amounts of controllable swelling strains at saturation when exposed to an aqueous saline environment. The volume fraction of the hydrophobic methyl methacrylate monomer to the hydrophilic acrylic acid monomer strongly influenced the swelling behavior of the copolymer. Two different cross-linking agents, allyl methacrylate and diethylene glycol dimethacrylate, were evaluated for their effectiveness in cross-linking and limiting the saturated swelling levels. The influences of the amounts of cross-linking agents and other processing parameters on the swelling behavior of the copolymer were studied using differential scanning calorimetry measurements, solubility tests, and swelling measurements in saline solutions. These measurements provided a good understanding of the structure of the copolymer, the effectiveness of the cross-linkers, the swelling mechanisms in this system, and the factors that strongly affect the swelling weight gain levels in this copolymer. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

Interest in swelling-type biocompatible structural materials began circa 1978 with the introduction of the concept of swelling-type bone implants by Kamel and coworkers.¹ These swelling-type implants were proposed as means of enhancing the fixation characteristics of implants in bone. The concept involved swelling of the implant by absorption of body fluids and achieving fixation at the implant–bone interface by an expansion–fit mechanism. Although research on the swelling-type implants began a long while ago, exploitation of this innovative concept has been largely hampered by the inability to produce a material with the desired hygro-mechanical properties. The de-

sired characteristics include controllable swelling strains (to accommodate differences in bone structure and properties from person to person depending on age and other factors), a fairly short time to achieve half the saturated swelling strain (this determines how long the patient has to be bedridden); low loss of mechanical properties with swelling; elastic stiffness close to that of bone (high stiffness of current metallic implants is known to cause bone resorption due to stress shielding); and excellent failure resistant properties.

Initial attempts at producing a material with the desired characteristics led to the development of a cross-linked porous polyacrylic acid–alumina composite.¹ Polyacrylic acid (PAA) is known to be a hydrophilic biocompatible polymer with very high swelling strains. Cross-linking and nanoscale alumina particles were introduced to limit the swelling strains and stabilize the polymer and to provide the required elastic stiffness in the dry

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state. Plugs of this composite were implanted in animals, and favorable bone remodeling response was documented.¹ However, mechanical tests in dry and saturated conditions revealed high losses in both strength and modulus with swelling, making this composite unsuitable for structural bone implants (implants that are expected to carry loads in service). Consequently, the use of these composites was mainly restricted to dental implants.² Kamel and coworkers, in later years, proposed an alternative mode of stabilizing polyacrylic acid using a three-dimensionally braided preform of graphite fibers³ as the reinforcement in the place of alumina particles. Mechanical tests on the three dimensionally braided graphite-polyacrylic acid composite in dry and saturated conditions once again revealed high losses in both strength and modulus with swelling.

In recent years, Ahmad and Kalidindi⁴ have attempted to stabilize the PAA matrix in the three-dimensionally braided graphite-polyacrylic acid composite by copolymerizing acrylic acid (AA) with methyl methacrylate (MMA). The idea of limiting the swelling strains in a hydrophilic polymer by copolymerizing it with a hydrophobic polymer has been used extensively in hydrogels and other interpenetrating polymer networks (IPNs) and semi-IPNs.⁵⁻⁹ The use of free radical polymerization, good miscibility, and close reactivity ratios of MMA and AA have been assumed to produce a random copolymer with fairly uniform composition. Preliminary swelling measurements and mechanical tests on braided composites using poly(MMA-AA) copolymer as the matrix indicated that this new composite exhibits overall volumetric swelling strains of about 2-3% and only about 10-20% loss of modulus and strength, which are in the acceptable range for the proposed application. Furthermore, both the swelling strain and the decrease in mechanical properties can be further controlled through matrix composition and cross-linking. Because of the promise seen in the preliminary mechanical studies, it was decided to undertake a detailed study to characterize the structure and swelling behavior of the cross-linked poly(MMA-AA) copolymer (without any fibrous reinforcement).

This paper presents the results of the detailed characterization study on the cross-linked poly(MMA-AA) copolymer along with the relevant synthesis details. The structure of the copolymer was mainly characterized through a series of differential scanning calorimetry (DSC) measure-

ments and solubility tests. We have also conducted a detailed study of the swelling behavior of the cross-linked copolymer. An excess saline solution was used as the solvent in the swelling studies because it closely reproduces the environment in the human body. The influence of the ratio of hydrophilic component to the hydrophobic component in the copolymer, the type and amount of cross-linking agent, and the temperature on the swelling levels and the swelling rate in the copolymer have been examined. Two different cross-linking agents, allyl methacrylate (AMA) and diethylene glycol dimethacrylate (DEGDMA), have been employed in this study. AMA was chosen based on the previous studies of Kamel and coworkers,¹⁻³ which showed that AMA is an effective cross-linking agent for PAA polymer systems polymerized in bulk. DEGDMA, on the other hand, has been widely used in cross-linking a variety of acrylic polymeric systems and has the added advantage of a symmetric structure with reactivity similar to that of AA and MMA monomers. The cross-linking efficiencies of these two cross-linkers for poly(MMA-AA) was evaluated.

POLYMER SYNTHESIS

The polymeric system studied is comprised essentially of a methyl methacrylate (MMA) backbone with varying amounts of acrylic acid (AA) comonomer to provide certain water affinity. The introduction of allyl methacrylate (AMA) or diethylene glycol dimethacrylate (DEGDMA) as cross-linking agents results in the formation of a three-dimensional network. A list of the monomers used in this study, along with some of their chemical and physical properties, is given in Table I. All these chemicals were purchased from Aldrich Chemical Co., Milwaukee, WI, and used as-received without any further purification. The polymerization was carried out in bulk, using a free radical mechanism with 2,2'-azobis 2,4-dimethylvaleronitrile (obtained from E. I. Dupont de Nemours & Co., Wilmington, DE) as the initiator. The initiator was added to varying volumetric ratios of MMA/AA monomers and mixed thoroughly. The desired amount of cross-linking agent (AMA or DEGDMA) was added to the mixture and manually stirred for ten minutes before polymerization. In all cases, the amount of initiator was fixed at 0.4 g/100 mL of total mixture. The polymerization

Table I Details of Monomers and Cross-linking Agents Used in This Study

Material	Density (g/cc)	Formula Weight (g/mol)	Concentration (%)	Molar Volume (cc/mol)
MMA	0.936	100.12	99	9.255
AA	1.051	72.06	99	14.439
AMA	0.938	126.16	98	7.286
DEGDMA	1.082	242.27	95	7.243

was carried out in a sealed water bath, which provided a uniform and accurate temperature control. The reaction mixture was poured into glass tubes, sealed with parafilm paper, and placed vertically in a glass stand inside the water bath. The assembly was maintained at 30°C for 5 h, then the temperature was raised gradually (5°C/h) to 70°C and kept at that temperature for 10 h, followed by overnight cooling (this heating cycle will be referred to as primary curing in the rest of this article). The tubes were then taken out of the bath and broken under slight clamp pressure. The samples were then removed from the glass tubes (no noticeable bonding to the tubes occurred) and placed in an oven in which the temperature was raised slowly (1°C/min) to 150°C and left for 3 h, followed by overnight cooling (this heating cycle will be referred to as post-curing in the rest of this article), thereby producing the desired cross-linked copolymer. The resulting samples were placed in a desiccator containing silica gel crystals to keep them dry until use.

It was observed that higher heating rates than the ones described above usually resulted in the formation of bubble-like domains in the upper parts of the samples during the primary curing cycle and the formation of uniformly distributed thin flakes during post-curing. Both defects disappeared completely when the heating cycles were performed at lower rates. In addition, white liquid clusters of various shapes and sizes were observed when the initiator was not dissolved completely in the monomer mixture. The clusters were found to be unreacted monomers which evaporated during post-curing leaving behind large porous sites. The fact that these clusters were unreacted monomers (not initiator) was ascertained from the smell of the liquid in these clusters and noting that the initiator used here is solid. The formation of these clusters was eliminated by thorough stirring and allowing enough time for the initiator to dissolve completely.

POLYMER CHARACTERIZATION

A variety of polymer samples with different ratios of AA, MMA, and cross-linking agent (AMA or DEGDMA) were synthesized using the procedure described in the previous section. All sample compositions used in this study are based on the volumetric ratios of the constituents in the monomer mix and are summarized in Table II. The homopolymer samples are designated by the polymer name (PMMA or PAA), followed by a number representing the volume of the cross-linker added to 100 mL of monomer and a letter representing the type of cross-linking agent used (A for AMA and D for DEGDMA). In a similar fashion, the copolymer samples are designated by the ratio of MMA/AA monomers in the monomer mix, followed by a number representing the volume of cross-linking agent added to 100 mL of the monomer mix and a letter representing the type of cross-linking agent used. The exact volumetric ratios and the corresponding molar ratios of these samples are also provided in Table II.

All synthesized samples exhibited high levels of transparency and appeared to be homogeneous without any noticeable cloud spots or segregations at the macroscopic level. While pure PMMA samples were colorless, pure PAA samples had a dark yellow color. The copolymer samples appeared yellow with the intensity of the color increasing with the amount of AA in the copolymer. In addition, it was noticed that the color contrast described above was evident only after the final post-curing cycle.

It has been reported that AMA is a fairly good cross-linker for PAA¹⁻³ and a relatively weak cross-linker for PMMA.¹⁰ It has also been reported¹⁰ that DEGDMA is a better cross-linker for PMMA than AMA. Therefore, one of the goals of this study was to examine the effectiveness of both AMA and DEGDMA as cross-linking agents for PMMA, PAA, and poly(MMA-AA) copolymer

Table II Compositions of Samples Used in This Study Based on the Ratios of the Different Components in the Monomer Mix

Sample	Vol %			Mol %		
	MMA	AA	CLA ^a	MMA	AA	CLA ^a
PAA [0]	0	100	0	0	100	0
50/50 [0]	50	50	0	39.06	60.94	0
PMMA [0]	100	0	0	100	0	0
50/50 [3A]	48.54	48.54	2.91	38.35	59.84	1.81
60/40 [3A]	58.25	38.83	2.91	48.09	50.02	1.89
70/30 [3A]	67.96	29.13	2.91	58.74	39.28	1.98
80/20 [3A]	77.67	19.42	2.91	70.44	27.48	2.08
90/10 [3A]	87.38	9.71	2.91	83.36	14.25	2.19
PAA [5A]	0	95.24	4.76	0	97.54	2.46
50/50 [5A]	47.62	47.62	4.76	37.89	59.12	2.98
60/40 [5A]	57.14	38.10	4.76	47.49	49.40	3.11
70/30 [5A]	66.67	28.57	4.76	57.97	38.77	3.26
80/20 [5A]	76.19	19.05	4.76	69.48	27.10	3.42
90/10 [5A]	85.71	9.52	4.76	82.15	14.24	3.59
PMMA [5A]	95.24	0	4.76	96.21	0	3.79
50/50 [7.5A]	46.51	46.51	6.98	37.34	58.25	4.41
50/50 [10A]	45.45	45.45	9.09	36.80	57.41	5.79
60/40 [10A]	54.55	36.36	9.09	46.05	47.90	6.04
70/30 [10A]	63.64	27.27	9.09	56.14	37.54	6.31
80/20 [10A]	72.73	18.18	9.09	67.18	26.21	6.61
90/10 [10A]	81.82	9.09	9.09	79.31	13.75	6.94
50/50 [15A]	43.48	43.48	13.00	35.76	55.79	8.45
60/40 [15A]	52.17	34.78	13.00	44.70	46.50	8.80
70/30 [15A]	60.87	26.09	13.00	54.43	36.39	9.18
80/20 [15A]	69.57	17.39	13.00	65.03	25.37	9.60
90/10 [15A]	78.26	8.70	13.00	76.65	13.29	10.06
50/50 [2D]	49.02	49.02	1.96	38.78	60.51	.71
60/40 [2D]	58.82	39.22	1.96	48.65	50.61	.74
70/30 [2D]	68.63	29.41	1.96	59.46	39.76	.78
80/20 [2D]	78.43	19.61	1.96	71.35	27.83	.82
90/10 [2D]	88.24	9.80	1.96	84.49	14.65	.86
PAA [5D]	0	95.24	4.76	0	98.55	1.45
50/50 [5D]	47.62	47.62	4.76	38.37	59.87	1.76
60/40 [5D]	57.14	38.10	4.76	48.11	50.05	1.84
70/30 [5D]	66.67	28.57	4.76	58.77	39.30	1.93
80/20 [5D]	76.19	19.05	4.76	70.49	27.49	2.02
90/10 [5D]	85.71	9.52	4.76	83.41	14.46	2.13
PMMA [5D]	95.24	0	4.76	97.76	0	2.24
50/50 [7.5D]	46.51	46.51	6.98	38.04	59.35	2.62
50/50 [8.5D]	46.08	46.08	7.83	37.90	59.14	2.95

^aCLA = cross-linking agent used; A = AMA; D = DEGDMA.

samples. The initial study of the cross-linker efficiencies was conducted through a series of dissolution/swelling tests on pure PMMA and PAA polymer as well as 50/50 poly(MMA-AA) copolymer samples synthesized with and without cross-linkers. The solvents used were an aqueous solution of NaOH in deionized water (0.5 g 100 mL) for PAA and a mixture of Toluene/Acetone (4 : 1 by volume^{11,12}) for PMMA. As expected, PAA and PMMA samples synthesized without AMA or DEGDMA dissolved completely in their corresponding solvents, while samples containing AMA or DEGDMA showed varying degrees of swelling, depending on the amount of cross-linker used. Similarly, the 50/50 copolymer samples synthesized without either cross-linker dissolved completely in both solvents while exhibiting varying degrees of swelling upon inclusion of AMA or DEGDMA. These tests were our preliminary indication of the effectiveness of both AMA and DEGDMA as cross-linking agents for the synthesized copolymer and a good determinant of the minimum amounts of AMA or DEGDMA needed to obtain effective cross-linking. In general, it was found that 2 mol % of AMA or 1 mol % of DEGDMA was enough to obtain typical swelling behavior in all systems without any indications of dissolution. Furthermore, the complete dissolution of the 50/50 uncross-linked copolymer in both solvents was a clear indication that the synthesized polymer is a true copolymer, not a mixture of two homopolymers.

DSC was used for measuring the glass transition temperatures of the synthesized samples. Figure 1 shows the normalized DSC traces for PMMA, PAA, and 50/50 poly(MMA-AA) polymer samples obtained using Perkin-Elmer thermal analysis system-Series 7. All traces shown are second runs on samples containing no cross-linking agent and obtained at a heating rate of 10°C/min. It has been reported⁶ that the first DSC runs in polymers containing hydrophilic groups may show a peak due to absorbed water molecules. This peak was found to disappear in second runs. Argon was used as the sweeping gas, and all samples weighed about 5 mg. All glass transition temperatures reported in this study were estimated from the thermographs using a built-in Perkin-Elmer TAS7 software package. The traces indicate that the glass transition temperatures for the synthesized PAA and PMMA uncross-linked homopolymers are 98 and 108°C, respectively. A single transition temperature of 103°C was detected

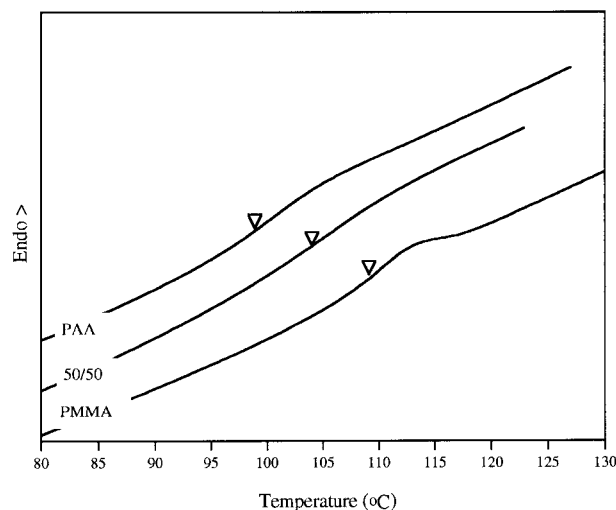


Figure 1 DSC traces of uncross-linked PAA, PMMA, and 50/50 copolymer.

for the 50/50 copolymer samples. These results confirm the formation of a single phase in the synthesized copolymer. Furthermore, the value of the T_g measured for the copolymer is in good agreement with the expected value computed from the T_g s of the constituent homopolymers using any one of relations used in current literature, such as the weighted average rule (by weight fractions) or the inverse weighted average rule. For example, the inverse weighted average rule,

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}, \quad (1)$$

where W_1 and W_2 are the weight fractions of the copolymer constituents, and T_{g1} and T_{g2} are their respective glass transition temperatures in K, provides an estimate of 105°C, which is in good agreement with the measurement.

In the case of cross-linked copolymers, the analysis of the glass transition behavior becomes complicated.¹³ It is generally known that in cross-linked systems, the softening temperature increases with cross-link density as a consequence of reduced segmental mobility.^{13,14} In addition, the glass transition behavior becomes less evident with cross-linking as a consequence of the reduction of the linear portion in the polymer structure. Both effects can be seen by comparing the DSC traces of the cross-linked copolymer samples shown in Figure 2 with those shown in Figure 1 for uncross-linked copolymers (both figures are

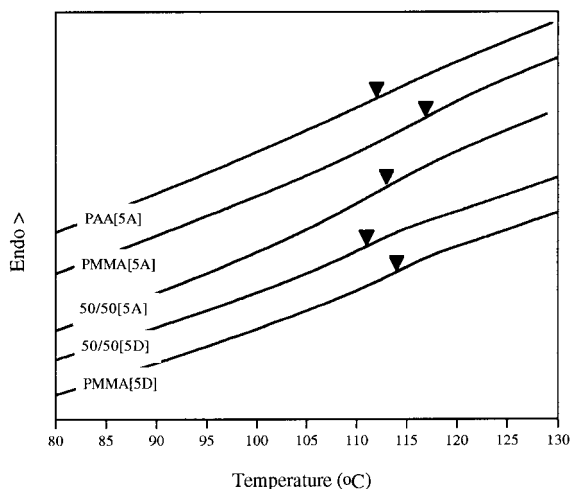


Figure 2 DSC traces of cross-linked PAA, PMMA, and 50/50 copolymer.

drawn to the same horizontal and vertical scale for comparison purposes and some of the traces are shifted vertically to avoid overlapping). The T_g values obtained from these measurements are summarized in Table III and were reproducible within two degrees.

Despite the difference in their hydrophilic/hydrophobic nature, MMA and AA monomers have similar reactivities.¹⁵ The same applies to the methacrylate functional group in AMA and DEG-DMA [see Fig. 3(a)]. It is assumed, therefore, that the three monomer units (MMA, AA, and the cross-linker) react in a random fashion depending on their molar ratios to form the main copolymer chains. Since all polymerization were carried out essentially to 100% conversion, the final composition of the copolymer is assumed the same as the comonomer ratios used. To confirm complete conversion, synthesized copolymer samples were crushed into powder and soaked at 100°C in a vacuum oven for six hours. No detectable weight loss occurred, indicating that no unreacted monomers were still left in the copolymer. Cross-linking between polymer chains is achieved by the extra functional groups in both cross-linking agents. In the case of AMA, this cross-linking is achieved by the allyl functional groups, which are known to have lower reactivities^{10,16} than acrylate and methacrylate groups in AA, MMA, and DEG-DMA monomers. This explains, in part, the relatively high amounts of AMA needed to achieve effective cross-linking. In addition, it was demonstrated through swelling measurements that this

cross-linking becomes more evident after the post-curing heat treatment cycle.

Based on the above discussion and supported by the DSC and the dissolution/swelling observations, the model shown in Figure 3(b) has been constructed to represent the synthesized cross-linked copolymer. Notice that the MMA and AA units are distributed randomly along the chains, and some cross-linker units are shown as not participating in the cross-linking process.

SWELLING BEHAVIOR

Thin circular discs (13 mm diameter and 1 mm thickness) were cut out of the bulk samples using a diamond saw, washed with methanol, and dried in an oven for six hours at 80°C before they were fully immersed in excess saline solution (0.9 g/100 mL NaCl concentration, Fisher Scientific, Pittsburgh, PA) for 200 hours at 25°C. The swollen disks were removed from solvent at various times, surface-dried using filter paper, and weighed using a digital scale with an accuracy of ± 0001 g. The exact dimensions of the samples were also measured using a digital micrometer with an accuracy of ± 001 mm. The percentage weight gain (%W) of the swollen samples at any instant during swelling is computed as

$$\%W = \left(\frac{W_t - W_0}{W_0} \right) \times 100, \quad (2)$$

where W_t and W_0 are the weights of the disk at time t and zero (the dry state), respectively. As swelling reaches equilibrium, %W approaches the

Table III Summary of the Glass Transition Temperatures of Synthesized Copolymer Samples with Different Compositions and Different Amounts of Cross-linking Agents

Sample	T_g (°C)
PAA [0]	98
PMMA [0]	108
50/50 [0]	103
PAA [5A]	111
PMMA [5A]	116
PMMA [5D]	114
50/50 [5A]	112
50/50 [5D]	111

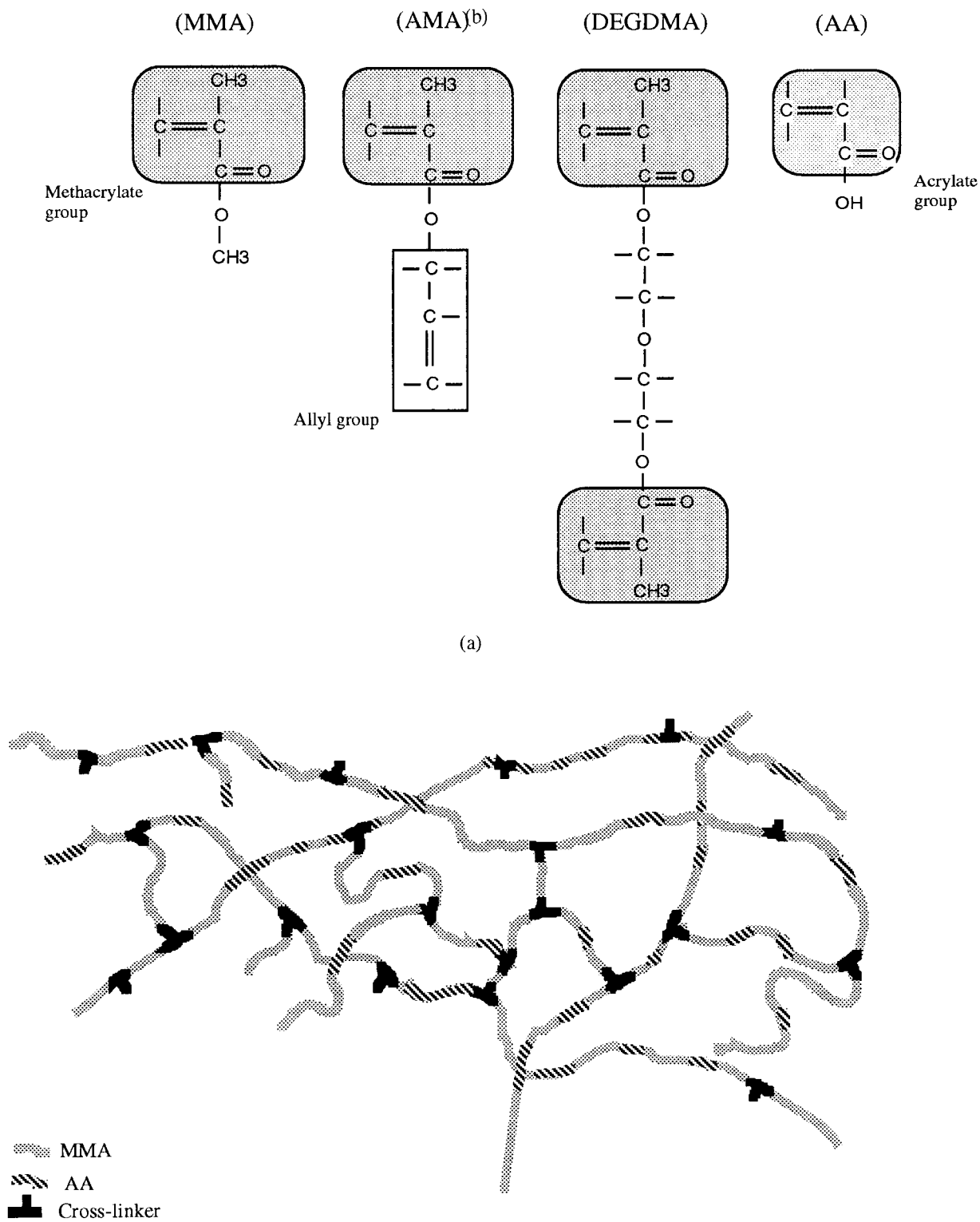


Figure 3 (a) Chemical structure of the monomers used in this study showing the reactive groups involved in the polymerization process. (b) A simplified model for the structure of the synthesized cross-linked copolymer.

saturated swelling, otherwise known as the equilibrium solvent content, $\%W_{eq}$. Similarly, the percentage change in volume ($\%V$) of the swollen samples is given by

$$\%V = \left(\frac{V_t - V_0}{V_0} \right) \times 100, \quad (3)$$

which can be calculated from $\%W$ assuming volume additivity^{1,5,7,17,18} of the polymer and the solvent in the swollen samples using

$$\%V = \left(\frac{\rho_m}{\rho_s} \right) \%W, \quad (4)$$

where ρ_m and ρ_s are the densities of the dry copolymer and the solvent, respectively. All swelling measurements reported in this study are based on weight gain measurements ($\%W$) as obtained from eq. (2). Nevertheless, the validity of eq. (4) in calculating the percentage change in volume from the percentage change in weight was confirmed experimentally [by comparison with eq. (3)] for several sets of measurements.

The primary objective of the swelling experiments is to study the influence of the hydrophilic/hydrophobic ratios and the amount and type of cross-linker on the swelling behavior of the synthesized copolymer in saline solution. The differ-

ent compositions of the samples used in the swelling measurements are included in Table II. Three samples of each composition were used in each set of measurements, and the scatter within each set was very minimal (within 3% of the average weight gains).

Effect of Hydrophilic/Hydrophobic Ratio

Figure 4 shows typical swelling curves generated for a series of swelling measurements conducted on samples containing varying ratios of MMA/AA but identical amounts (vol %) of AMA. These curves clearly show the significant effect of increasing the relative amount of AA in increasing the swelling levels of the synthesized copolymer. The copolymers in this figure exhibit similar time scales in approaching equilibrium. Generally, half of the saturated weight gain was achieved in the first 24 h after immersion, and the saturation weight gain was reached in about 100 hours. Further swelling, after the first 100 hours was very slow and stopped practically after about 200 hours. No noticeable effect of the MMA/AA ratio on the swelling time scale described above was observed.

Similar results as described above were obtained from samples with DEGDMA as the cross-linker, except for the values of saturated swelling.

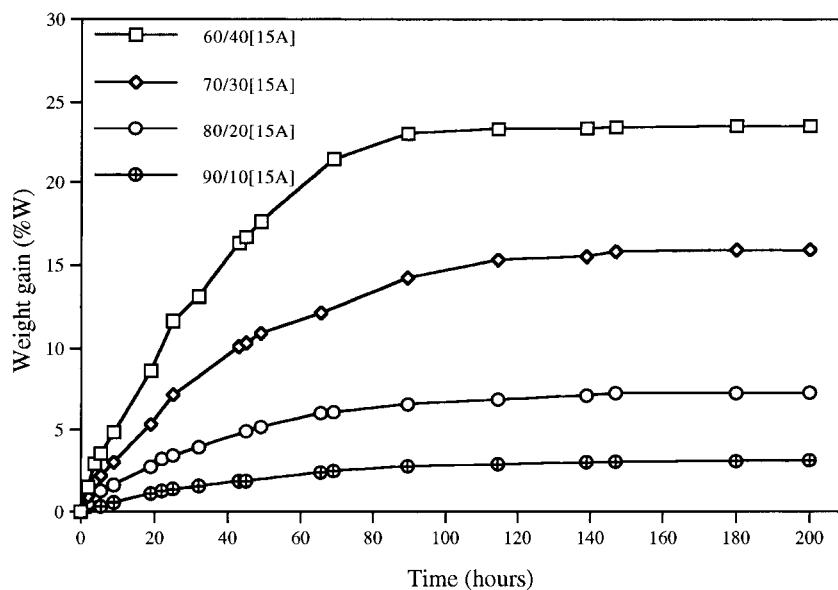


Figure 4 The effect of AA content on the swelling behavior of AMA cross-linked copolymer.

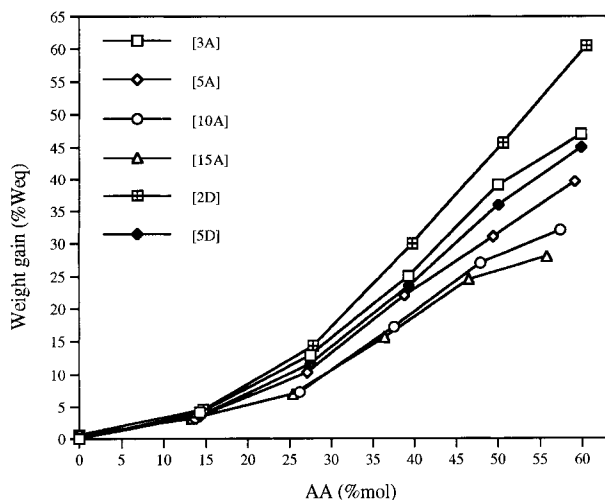


Figure 5 The effect of AA content on the saturated swelling levels.

Figure 5 shows the effect of the relative amount of AA (mol %) on the saturated swelling values for different amounts of the two cross-linkers used in this study. Notice that each solid line represents one series of swelling measurements on samples containing varying ratios of MMA/AA but identical amounts of the cross-linker (vol %). All curves shown in Figure 5 indicate a monotonic increase in saturated weight gain with increase in the relative amount of AA in the copolymer. Furthermore, this relationship is observed to be fairly linear for moderate amounts of AA (greater than 25 mol % and less than 50 mol %) in the copolymer. Some nonlinearity is also observed in all these curves, especially at low mol % of AA in the copolymer. We believe that these nonlinearities are attributable to some or all of the following reasons.

1) Although we have qualitatively demonstrated that both cross-linkers can effectively cross-link either homopolymers through the solubility and DSC measurements, their cross-linking efficiencies for MMA and AA are not expected to be exactly identical. Consequently, the efficiency of either of the cross-linkers in cross-linking the synthesized copolymer is expected to change with MMA/AA ratio in the copolymer.

2) The molar ratio of the cross-linker in each of the curves in Figure 5 is not exactly the same as can be seen from Table II, since the samples in each series were synthesized with constant volume ratios of cross-linker.

3) The complex nature of the distribution and interactions of the monomers involved can change with their ratios in the monomer mix, producing a non-linear influence on the saturated swelling of the synthesized polymer network.

Effect of Cross-linker

The swelling curves obtained from a series of samples containing identical MMA/AA ratio but varying amounts of AMA are shown in Figure 6. It is apparent from Figure 6 that increasing the ratio of cross-linker reduces the saturated swelling levels of the copolymer without affecting the time needed to reach saturation. Similar behavior and time-scale was previously reported by Kamel and coworkers¹⁻³ for AA/AMA systems.

To further investigate the effectiveness of both cross-linkers in controlling the swelling behavior of the copolymer, the saturated swelling measurements were plotted against the molar percentages of cross-linker for both AMA and DEGDMA, as shown in Figure 7. Notice that each solid line in this case represents a series of swelling measurements on samples containing fixed ratio of MMA/AA and varying amounts of cross-linker. All plots show an asymptotic decrease in the saturated swelling levels with the mol % of cross-linker. No significant reduction in saturated swelling levels was obtained when the amount of AMA was increased beyond 6 mol %. Furthermore, it can be seen from Figure 7 that for the same molar percentages, DEGDMA is only slightly more effective in cross-linking the synthesized copolymer than AMA, as indicated by the slightly lower saturated swelling values obtained at identical molar percentages of both cross-linkers. However, when the saturated swelling levels are plotted for constant volume ratio as shown in Figure 5 (instead of the molar ratio used in Figure 7), it can be seen that AMA is slightly more effective than DEGDMA (see the [5A] and [5D] curves in Figure 5).

Diffusion Measurements

In addition to the equilibrium degree of swelling, the rate at which equilibrium is reached and the transport mechanism of swelling are of great importance in the intended application. In the simplest case, where the transport mechanism is Fickian, the rate of approaching equilibrium is characterized by the diffusion coefficient D . The value of D can be obtained from the plots of the

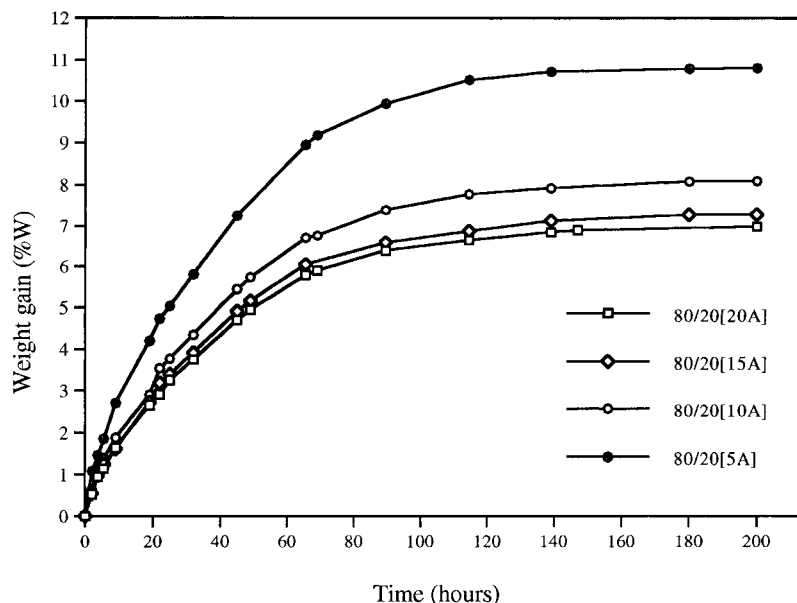


Figure 6 The effect of the amount of cross-linking agent (AMA) on the swelling behavior of 80/20 cross-linked copolymer.

degree of saturation ($\%W/\%W_{eq}$) against \sqrt{t}/L , where t is the time, and L is the initial thickness of the specimen. The linearity of the initial portion of the plot ($\%W/\%W_{eq} < 0.6$) is an indication of

Fickian diffusion mechanism, and the diffusion coefficient can then be determined from the slope of the linear portion using

$$\frac{\%W}{\%W_{eq}} = \sqrt{\frac{D}{16\pi L}} \sqrt{t} \quad (5)$$

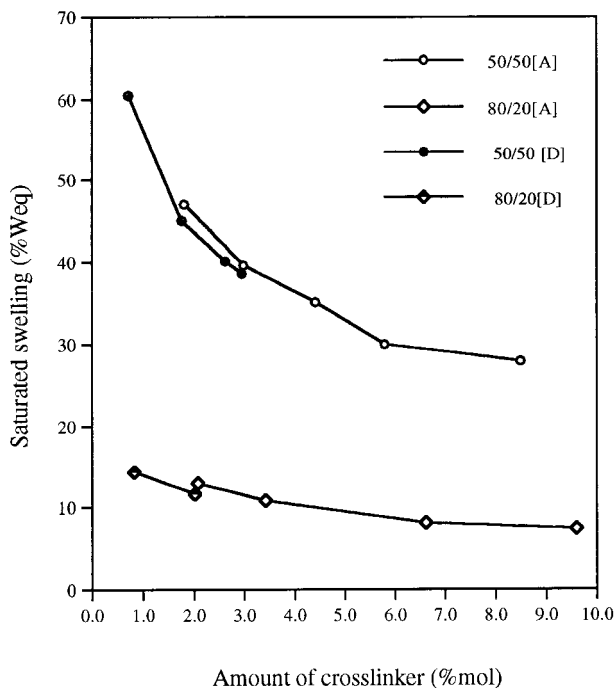


Figure 7 The effect of the amounts of the two cross-linking agents on the saturated swelling.

It has been reported that both the amount of cross-linker and/or the hydrophobic/hydrophilic balance can have a significant effect on the absorption rate and/or mechanism in some cross-linked polymer networks.^{5,19,20} Figure 8 shows the diffusion plots generated for two series of swelling measurements in which the amount of cross-linker and the MMA/AA ratio are systematically varied. It is apparent from these figures that all curves are virtually identical and overlap for the major part of the swelling history. This clearly indicates that neither the amount of the cross-linker nor the hydrophobic/hydrophilic ratio has a significant effect on the sorption rate in the synthesized polymer. In addition, all curves show a high degree of linearity in the initial portions ($\%W/\%W_{eq} < 0.5$), indicating that the diffusion mechanism is Fickian. The values of D obtained at room temperature for all samples in our study were in the range $4.7\text{--}5.4 \times 10^{-9} \text{ cm}^2/\text{s}$. It should be noted that these values are roughly an order of magnitude higher than those reported for epoxy

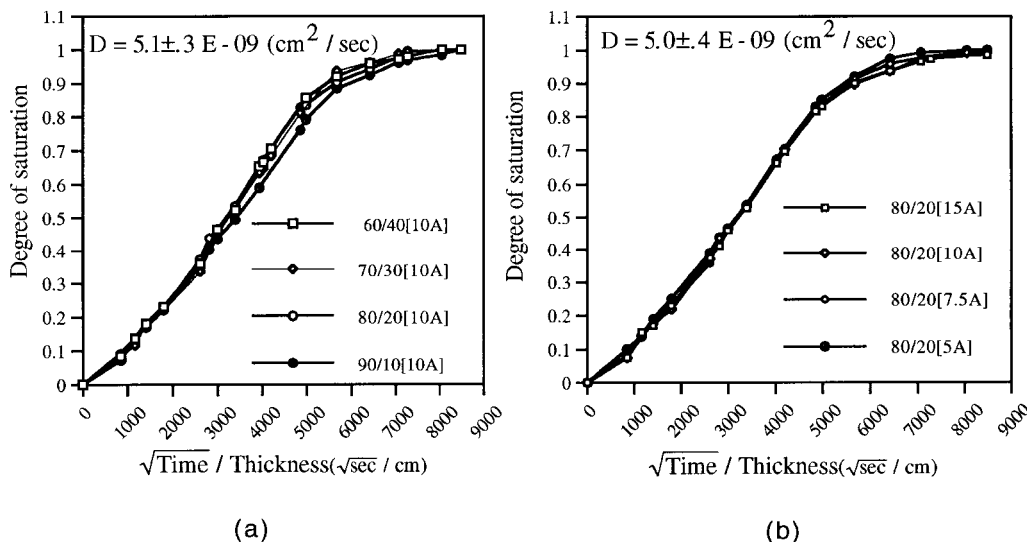


Figure 8 (a) The effect of AA content on the diffusion coefficient (D). (b) The effect of the amount of cross-linking agent on the diffusion coefficient (D).

resins²¹ and at least an order of magnitude lower than those for highly swellable hydrogels.^{5,9,22}

Effect of Temperature

The effect of temperature on the swelling behavior of the synthesized copolymer is studied on three sets of samples with 70/30[10A] composition at temperatures of 25, 40, and 60°C. The swelling curves are shown in Figure 9, and the corresponding diffusion plots are shown in Figure 10. The results indicate that raising the temperature of the swelling media has a significant effect on both the saturated swelling and the absorption rate (characterized by the diffusion coefficient). The diffusivities (D) of the swollen samples, derived from the initial slopes of the curves, obeyed an Arrhenius behavior, which can be represented by the expression

$$D = .0451 \exp\left(\frac{-39580}{RT}\right) (\text{cm}^2/\text{s}) \quad (6)$$

where R is the gas constant, 8.31 J/mol-K, and T is the absolute temperature in K.

It can also be seen from Figure 9 that the saturated swelling increases with temperature in the range of temperatures tested here. Furthermore, the increase in saturated swelling level between 40 and 60°C is fairly small compared to the increase between 25 and 40°C.

The effect of temperature on swelling has been extensively studied in IPN hydrogels. It has been reported in literature^{7,20,23,24} that the effect of temperature on the swelling behavior can be explained in terms of

1. The polymer–solvent interactions, such as the association and disassociation of hydrogen bonding between water and the pendant hydrophilic side groups,
2. polymer–polymer intermolecular and intramolecular hydrophobic interactions among side groups; and
3. chain relaxation and the mobility of the side groups in the polymer network.

It is conceivable that some or all the mechanisms mentioned above may be present to a certain extent in the copolymer studied here and perhaps could explain the observations in Figures 9 and 10. However, we have not pursued such a detailed study on the temperature effects since it is not relevant to the currently intended application (that of bioimplants) for this copolymer.

CONCLUSIONS

A new cross-linked poly(MMA-AA) copolymer has been successfully synthesized for potential applications in bioimplants. The saturated weight gain

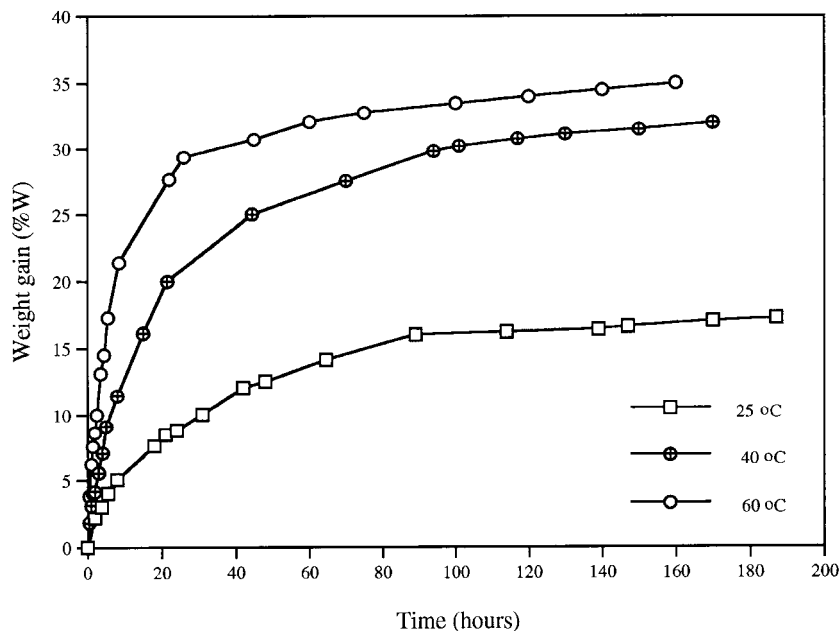


Figure 9 The effect of temperature on the swelling behavior of 70/30 [10A] copolymer.

of this hydrophobic/hydrophilic system can be adjusted to a wide range of values by varying the MMA/AA ratio or the amount of cross-linker in the monomer mix. Both cross-linkers investigated (AMA and DEGDMA) were found to be effective in cross-linking the copolymer with similar cross-linking efficiencies. The absorption mechanism

was observed to be mainly Fickian diffusion. Neither the MMA/AA ratio nor the amount of cross-linkers showed any significant influence on the room temperature diffusion coefficient or the diffusion mechanism. The diffusion coefficient was found to obey Arrhenius dependence of temperature with $D_0 = 0.0451 \text{ cm}^2/\text{s}$, and $Qd = 39.6 \text{ kJ/}$

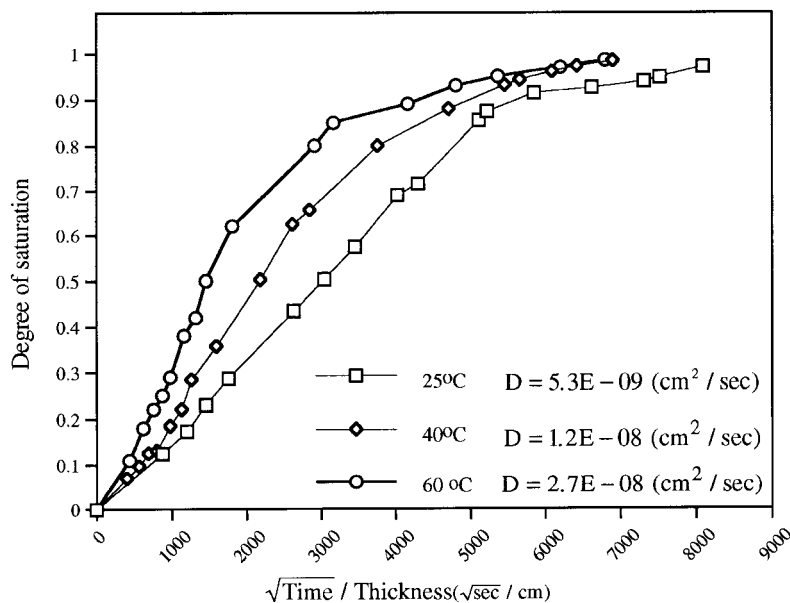


Figure 10 The effect of temperature on the diffusion coefficient (D) in 70/30 [10A] copolymer.

mol. The room temperature diffusion coefficient in this copolymer was about $5.1 \times 10^{-9} \text{ cm}^2/\text{s}$.

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