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MECHANICAL PROPERTIES OF CROSSLINKED POLY(METHYL METHACRYLATE) POLYMERS UNDER SPACE ENVIRONMENTAL CONDITIONS

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I INTRODUCTION

This sixth Quarterly Technical Summary Report describes work conducted for the National Aeronautics and Space Administration under Task Order NASr-49(13) during the contractual period December 1, 1964 to February 28, 1965. The program is monitored by the Ames Research Center of NASA.

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The objective of this study of crosslinked poly(methyl methacrylate) (PMMA) polymers is to obtain information on the behavior of crosslinked polymers in space environments. Of particular interest are the degradative changes in structure which take place *in vacuo* at elevated temperatures, the kinetics associated with the degradation process, and the influence of the degradative changes on the mechanical properties of the polymer.

During the report period, tensile stress-strain data were obtained on the new Polycast Corporation samples at 165 and 185°C, and a new computer program was written to analyze these data.

The continuous and intermittent stress relaxation was measured on uncrosslinked PMMA and on two of the more highly crosslinked samples at temperatures between about 170 and 225°C, both in air and in vacuum.

To obtain an estimate of the degree of crosslinking and to characterize further the samples, swelling measurements were carried out in two solvents.

Author

II TENSILE STRESS-STRAIN CHARACTERISTICS OF UNCROSSLINKED AND CROSSLINKED PMMA

During the previous report period, Instron tests were conducted at 145°C at crosshead speeds of 20, 10, 5, 2, 1, 0.5, 0.2, and 0.1 inches/minute. Similar runs at 165 and 185°C were carried out during the current period. The lots tested were 1, 2, 3, 4, 5, 9, 11, and 12. Lot 9 is another sample of uncrosslinked PMMA, identical with Lot 1, and was substituted for Lot 10 because of an error in labeling on the part of the manufacturer. Subsequently, rings have been cut from Lot 10 and will be tested during the next report period.

The installation of a Burroughs 5500 computer at the Institute required writing of a new program for deriving stress-strain data from the Instron traces. The new program contains two major improvements: (1) Specimen dimensions are now calculated at test temperature, using the thermal expansion coefficient of specific volume. (2) The (average) strain ϵ is now calculated from the exact equation[1]

$$\epsilon = \frac{4\Delta L}{\pi(D_o+D_i)} - \frac{D_o-D_i}{D_o+D_i}\left[1-(1+\epsilon)^{-\frac{1}{2}}\right] \qquad (1)$$

where ΔL is the crosshead displacement and D_o and D_i are the outer and inner diameters of the rings.* Previously the second term on the right-hand-side of Eq. (1) was omitted. The corrections now incorporated are minor but they improve the accuracy of the data.

Analysis of the data revealed that Lots No. 4, 5, and 12 are too highly crosslinked for Instron testing using the ring method. They will be eliminated from future runs planned at several supplementary temperatures. Plots of the data will be made after completion of the tests.

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*Equation IV-9 of Ref. 1 contains an erroneous factor of 1/2 in the second term on the right of the equation.

III STRESS RELAXATION

The continuous and intermittent stress relaxation was determined on uncrosslinked PMMA (Lot 1), and on Lots 2 and 3, crosslinked with ethylene glycol dimethacrylate (EDMA).* The tests were carried out both in air and in vacuum.

A. Experimental Procedure

Experiments under vacuum were carried out in the vacuum relaxometer described in previous reports. Tests under atmospheric conditions were made in a modification of an apparatus described in detail elsewhere.[1] Since the experimental procedures used with both instruments have now been well established, they are detailed in this section for convenience.

Previously, rectangular strip specimens about 4 cm long and 0.5 cm wide were used. Difficulty was encountered in mounting these specimens without exerting forces on the load cells at the beginning of a run. Because the specimens were held rigidly between the clamp on the load cell and the clamp on the extending rod, thermal expansion caused a deflection of the load cell beams before a run was begun. Although the load cells are temperature-compensated as well as possible, there is still a substantial residual unbalance over large temperature ranges. The effect of this thermally induced change in the zero point combined with that from the bridge unbalance caused by expansion of the specimen, and there was no reliable means to separate the two effects. Another difficulty with the strip specimens was their tendency to break near the lower clamp during a run.

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*Because of an error in the value supplied, the amount of crosslinker in Lot 2 and Lot 10 was erroneously stated in Table I of the previous report. The correct amount is 0.25% w/w. The corrected number of moles of effective chains per cc is given in Table II of this report.

The problems of specimen failure and thermal drift were both remedied by modifying the relaxometer to accommodate ring specimens. Specimens used had an outside diameter of about 1.185 inches, an inside diameter of about 1.075 inches, and a thickness of about 0.036-0.040 inch. The rings are not mounted rigidly but are suspended between mandrels attached to the load cells and extension rods at each station. The specimens are mounted so that at ambient temperature they hang over the upper mandrel (on the extension rod) and just touch (but exert no force upon) the lower mandrel (attached to the load cell). When thermal equilibrium has been reached at the test temperature, the ring hangs freely over the upper mandrel, but it no longer touches the lower mandrel because the expansion coefficient of the specimen is greater than those of the metals of which the apparatus is constructed. The thermal drift of the load cell is now readily balanced out before the ring is extended. Both the accuracy and reproducibility of force measurements have been greatly improved by this procedure, and the rings have seldom been observed to fail at the clamps.

1. Atmospheric Tests

The apparatus used for studies in air at atmospheric pressure contains two load cells mounted at the bottom of the apparatus framework. Above each load cell an extension rod runs through the top of the framework to adjustable stops and a take-up mechanism consisting of a rack-and-pinion driven by a worm gear. The specimen ring is suspended between mandrels attached to the extension rods and load cells. Turning the worm gear with a hand crank extends the rings. The framework may be removed from the heating chamber for sample installation. The output of the left load cell is run to a Brown recorder having a 1 mv full-scale input. The right load cell output is measured with a Rubicon potentiometer.

Before a run the load cells are calibrated using known weights. The specimens are mounted, and the stops are adjusted to give the desired extension. The chamber is preheated to the test temperature and the apparatus with mounted specimens is installed. About 30 minutes is required for the samples and apparatus to reach thermal equilibrium at the test temperature.

The left specimen is then extended relatively slowly (over a period of 10-15 sec) using the hand crank while the force is monitored on the Brown recorder.

Intermittent measurements are begun on the right specimen as soon as possible after the continuous measurement is under way. The specimen is extended in the same way as the left specimen and the load-cell output is measured with the potentiometer. The specimen is returned to its zero-strain configuration about 15 sec after being extended. Temperature is measured periodically with a thermocouple placed between the specimens.

2. Tests Under Vacuum

Tests are carried out in the vacuum relaxometer according to the following procedure: Immediately before a run, each of the three load cells is calibrated at ambient temperature by hanging a known weight on the end of the beam and noting the pen deflection on the Offner recorder. The specimens are cleaned with a cotton swab saturated with ethanol to remove surface contaminants, then weighed and mounted in the relaxometer. The metal cover is placed over the relaxometer and the chamber is evacuated for several hours (usually overnight) before a run is made.

The thermostatted molten salt bath in which the vacuum chamber is to be immersed is preheated to 20-40 degrees above the test temperature. The run is begun by raising the bath around the chamber, which then absorbs heat and lowers the bath temperature. When the bath has cooled to the run temperature the thermoregulator is set and the specimen temperature is monitored closely until it is constant within a temperature range equal to the control range of the thermoregulator. The elapsed time from immersion of the vacuum chamber until thermal equilibration of the specimens has been achieved is from 1-1/2 to 2 hours.

Pressure in the chamber increases when the temperature is raised to the test temperature; it then decreases continuously during the remainder of the run. The maximum pressure read on the Pirani gauge is typically 10-15 μ (immediately after immersion) and decreases rapidly to 3-5 μ by the time the samples have come to thermal equilibrium. Further decreases to 0.1-1 μ are typical.

At the beginning of a run the center specimen is extended slowly (over a period of 10-20 sec) until the desired stress or strain is achieved, and the exact extension is measured with a cathetometer. The thumbscrews on the data bar are tightened, thus limiting the extension of the remaining specimens to an amount equal to that of the center specimen. The specimen which is to be stressed continuously (usually the one mounted at the left load cell) is then extended rapidly (in < 0.1 sec) by the preset amount, and the force is recorded continuously until it either is constant or changes slowly with time.

Intermittent measurements on the remaining specimen are begun within a few minutes after the continuous measurement is started. These are made by extending the specimen rapidly by the preset amount, holding it in the extended position for a short time while measuring the force on the recorder, then returning the specimen to its initial unstressed position. Intermittent measurements are repeated for the remainder of the run at approximately equal logarithmic elapsed time intervals. Force measurements for the continuously extended specimen are obtained simultaneously by using the second channel of the recorder.

During the course of a run the temperature of six thermocouples inside the chamber is checked periodically, giving both the distribution of temperatures over the chamber and their change with time. Repeated checks of the distribution, including measurements with one thermocouple touching one of the metal extension rods, showed the chamber temperature to be uniform within less than one degree.

3. Data Reduction

Although the relative positions of the load cell mandrel and extension rod mandrel are known accurately at ambient temperature, and the amount of extension at run temperature is measured, different thermal expansion coefficients for all the materials involved combined with relatively high load cell compliance make accurate calculation of the strain difficult. This is not presently a serious problem, since the results are expressed as force relative to the force when the specimen was first extended $f(t)/f(o)$. Several workers[1,4] have shown that $f(t)/f(o)$ is independent of strain over an extended range. Methods for calculating

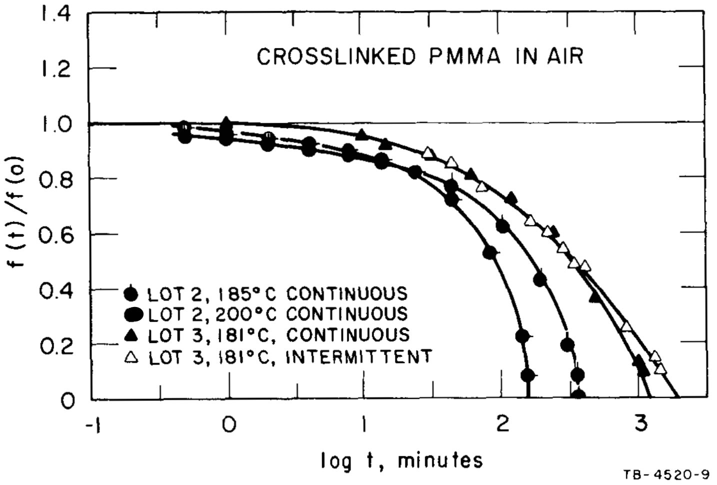

FIG. 1 CONTINUOUS AND INTERMITTENT STRESS RELAXATION OF CROSSLINKED PMMA IN AIR

the actual strain from thermal expansion coefficients of the specimen and apparatus and the load cell compliance are being studied. For the results reported here, all specimens were extended by the same amount (as measured with a cathetometer) after coming to thermal equilibrium.

Results are analyzed in several steps. First the outside diameter and weight of the ring are used to calculate the thickness T and inside diameter of the ring.[2] Thermal expansion of the specimen from ambient to the glass transition temperature is calculated by means of

$$L_{Tg} = L_{25}[1 + \rho_{25}(T_g - 25)(\beta/3)] \tag{2}$$

where L is any dimension of the specimen (such as thickness or diameter) and the subscript refers to the temperature, while ρ is the density, and β is the expansion coefficient of specific volume below T_g. Once the dimensions at T_g are known, magnitudes at the run temperature T_r are calculated from

$$L_{Tr} = L_{Tg}[1 + \rho_{Tg}(T_r - T_g)(\alpha/3)] \tag{3}$$

where α is the expansion coefficient of specific volume above T_g.

The cross-sectional area A of the sample at run temperature is calculated from

$$A = (D_o - D_i)\, T, \tag{4}$$

where D_o and D_i are the outside and inside diameters of the ring.

Forces exerted on the sample during a run are calculated from the relation

$$f = csd, \tag{5}$$

where f is the force, c is the load cell calibration factor, s is the sensitivity setting of the recorder and d is the observed pen deflection.

The engineering stress σ may then be determined from

$$\sigma = f/A, \tag{6}$$

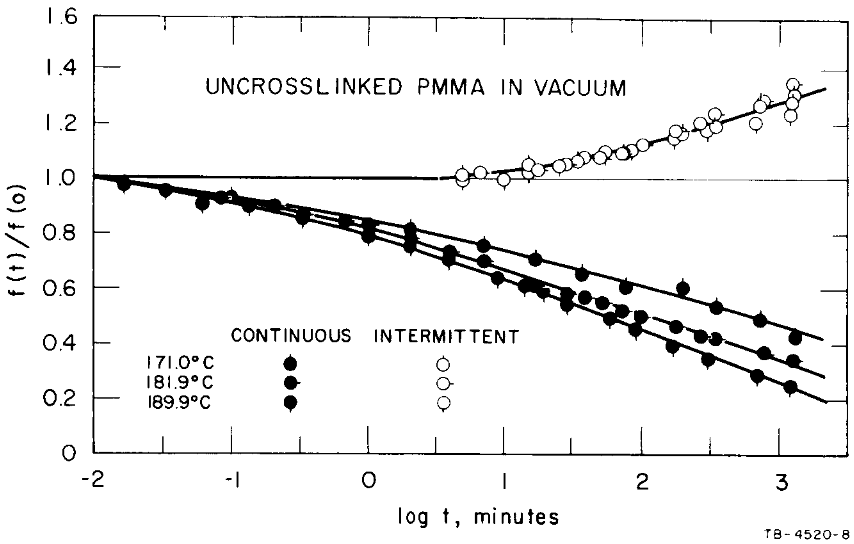

FIG. 2 CONTINUOUS AND INTERMITTENT STRESS RELAXATION OF UNCROSSLINKED PMMA IN VACUUM

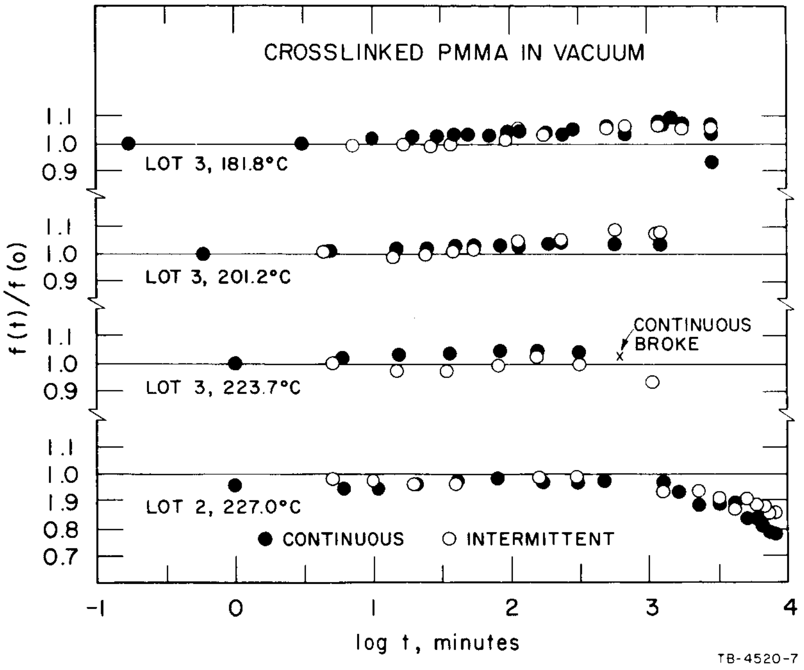

FIG. 3 CONTINUOUS AND INTERMITTENT STRESS RELAXATION OF CROSSLINKED PMMA IN VACUUM

but results are more often plotted as f(t)/f(o) vs. log t, where f(t) is the force at time t and f(o) is the initial force.

B. Results

Results of air runs on Lot 2 at 185°C, Lot 2 at 200°C, and Lot 3 at 181°C are shown in Fig. 1. Several features are immediately apparent. First, the force decays from its initial value to zero in all three cases. The rate of decay is faster at higher temperatures, as a comparison of the 185 and 200°C runs on Lot 2 shows. For Lot 3 at 181°C, the continuous and intermittent measurements are almost identical within experimental error. Lot 3, which is more highly crosslinked than Lot 2, degrades more rapidly at a nearly equivalent temperature.

That extensive degradation occurred was also evident from the appearance of the specimens after a run; they were slightly discolored, distorted, brittle, and filled with small bubbles. In some cases specimens melted into a pile which stuck to the lower mandrel. Weight losses could not be determined because of the impossibility of collecting all of a specimen after a run.

The strains used for the runs shown in Fig. 1 are not known accurately for reasons described in detail in the previous section. The runs on Lot 2 were made at approximately 20% extension, and the run on Lot 3 at about 10% extension. Other attempts to make runs at higher strains showed that extending the specimen more than 20% is likely to cause rupture at elevated temperatures. A specimen of Lot 3 at 185°C ruptured shortly after being extended 20%, as did a specimen of Lot 2 at 200°C after being extended 60%. As detailed ultimate property data were not available at the beginning of the series of tests, subsequent runs in both the vacuum and air relaxometer were made at nearly equal strains of about 10%. In this way, stress relaxation data at comparable strains could be obtained at different temperatures for specimens having different crosslink densities.

The results of continuous and intermittent measurements in vacuum on Lot 1 (uncrosslinked PMMA) at three temperatures are plotted as f(t)/f(o) vs. log t in Fig. 2. As one would expect, the stress relaxes more rapidly at higher temperatures in the continuous mode. The rise in f(t)/f(o) with an increase in time in the intermittent mode is unexpected and appears to reflect structural changes in the material. These changes are observed even at the lowest temperature of measurement, 171.0°C. An attempt was made to plot the continuous measurements as log $\sigma(t)$ vs. log t, superposing the results at the three temperatures in the customary way. This was not successful probably because of the structural changes indicated by the intermittent measurements, although the effect of some differences in the strains for the three runs cannot be ruled out.

Figure 3 gives the results of measurements on Lots 2 and 3, both of which are crosslinked with EDMA. The most striking feature of these runs is the lack of any appreciable stress decay at times up to about 1000 minutes (17 hours) or temperatures up to about 225°C. Both continuous and intermittent measurements remain nearly constant over a run, contrasting markedly with the measurements in air, where complete decay of the stress was observed over a similar time period. In the single case (Lot 2 at 227°C) where measurements were extended appreciably beyond 1000 minutes, both continuously and intermittently stressed samples showed definite signs of decay. However, in addition to having the longest duration, this run was made at the highest temperature so far attempted.

Both continuous and intermittent measurements on Lot 3 at all three temperatures either remain constant or increase slightly with time. An actual increase in the force on a continuously strained sample is impossible, and the apparent slight increase is attributed to drift in the recorder baseline. Two solutions to this problem are being considered: New potentiometers in the bridge-balancing circuit and an improved layout of all bridge components external to the apparatus itself. Also, in future runs the continuously stressed specimen may be released periodically to allow direct observation of the true baseline.

The slight increase in the force ratios for intermittent measurements is probably real, since by the nature of the measurement the baseline is observed each time a point is taken.

Despite the apparent lack of stress decay at temperatures so far investigated, the specimens do show some weight loss after a run. The relative amount of loss varies with both temperature and duration of a run, as shown in Table I.

TABLE I

TYPICAL SPECIMEN WEIGHT LOSSES IN THE VACUUM RELAXOMETER

Sample	Temperature (^{o}C)	Approximate Duration of run (hours)	Average Percent decrease
Lot 1	171.0	22	4.1
	181.9	21	6.7
	189.9	21	6.9
Lot 2	227.0	124	26.9
Lot 3	223.7	18	14.0

In contrast to the air runs, samples used in vacuum runs were only very slightly discolored and gave little appearance of degradation. At higher temperatures, small bubbles were discernible in the specimen.

C. Conclusions and Plans for Future Work

Work so far has indicated quite clearly that the thermal degradation of PMMA is stabilized by crosslinking and by vacuum. Grassie and Melville[3] studied the thermal degradation of EDMA-crosslinked and uncrosslinked PMMA *in vacuo* by measuring the flow rates of the evolved monomer in the gas phase, and concluded that degradation was a true depolymerization reaction ("unzipping"). For crosslinked PMMA they considered three possible mechanisms: (1) Initiation occurs at the ends of chains but proceeds only as far as the first crosslink in each chain; (2) unzipping proceeds past crosslinks along the main chain, i.e., without propagation of the depolymerization through the EDMA molecule; (3) when depolymerization reaches a crosslink it proceeds not only along the main chain but is also propagated to the adjacent chain.

Their experiments indicated that there was no essential difference in the rates measured on crosslinked or uncrosslinked PMMA, and that therefore the degradation in crosslinked PMMA followed mechanism (2). They also found that the degree of crosslinking had no effect on the rates.

Our experiments in air indicate that the degree of crosslinking might have an effect on the rate of chemical stress relaxation. The tests in vacuo are inadequate at this stage to decide this question. However, the fact that definite (and at the higher temperatures quite substantial) weight losses occurred without imparing the specimens ability to support stress, indicates that degradation might proceed according to mechanism (1). The observed behavior is consistent with the assumption that depolymerization leaves the essential network intact until the sol fraction (uncrosslinked chains) and all loose ends are eliminated. Crosslinks might therefore impose an energy barrier to the depolymerization reaction.

An essential difference between the vacuum experiments of Grassie and Melville and ours might be in the partial oxygen pressures achieved. The British workers did not state the degree of their vacuum. The partial pressure of oxygen in our tests was of the order of 0.3 to 1.0×10^{-6}atm. It is interesting to note in this regard that Tobolsky,[4] working with sulfur-cured rubbers, found that the oxygen pressure had to be below about 10^{-4} atm. before the rate of stress relaxation was markedly diminished.

The partial pressure of oxygen in the vacuum relaxometer may actually be lower than that calculated from the total pressure, since the copper housing may scavenge oxygen. A run using a glass housing jar instead of the copper can is planned to determine if this is the case.

A further possibility is that some material in the specimen which catalyzes degradation is outgassed in the period during which the specimens come to thermal equilibrium. A run in a helium atmosphere is planned to see if the absence of a vacuum on the specimen at any time in its history has an effect on the rate of degradation. The helium will be maintained at a pressure slightly above atmospheric to prevent entry of air into the system.

After the runs in the glass housing and in a helium atmosphere have been completed, runs will be made at the upper temperature limit of the apparatus to see if more rapid degradation can be induced.

Two improvements in data analysis are in progress. A computer program is being written to do all calculations, and methods are being studied for calculating the strain on a specimen from the expansion coefficients of the specimen and the expansion coefficients of the materials of which the apparatus is constructed. If a satisfactory method of calculating strain can be found it will be incorporated into the computer program.

New potentiometers will be added to the strain bridge circuitry to improve its stability. These will be incorporated into an improved layout of all other bridge components external to the strain gauges themselves.

IV SWELLING MEASUREMENTS

As an independent quantitative measure of the extent of crosslinking, swelling measurements were carried out on samples of Lots 2, 3, 4, and 5, all crosslinked with EDMA, and Lots 11 and 12, crosslinked with HDMA. Measurements on Lot 10 are under way. Two solvents were used: 1,2-dichloroethane and chloroform.

The experimental procedure was slightly different for the two solvents. For dichloroethane a sample was first weighed, then placed in about 100 ml of solvent at room temperature. The solvent was changed several times during a run, which was continued until the sample came to constant weight. Measurements could not be made by immersing the sample directly in chloroform, since this caused the sample to break up. Instead the specimen was weighed, placed for about an hour in refluxing n-butyl acetate, then placed in n-butyl acetate at 25°C. The sample of Lot 3 received a slightly different treatment in that it was left in refluxing n-butyl acetate for about 24 hours.

After standing about 5 days in n-butyl acetate, a sample was transferred to chloroform and the same procedure was used as for the dichloroethane. After coming to constant weight in the solvent, the samples were dried to constant weight in a vacuum oven at 130-165°C.

The number of moles of network chains per cc, ν_e, was calculated from[5]

$$\nu_e = \frac{-[\chi_1 v_2^2 + v_2 + \ln (1-v_2)]g}{[v_2{}^{1/3} g^{2/3} - v_2/2]V_1}$$

where χ_1 is the thermodynamic solvent-solute interaction parameter, V_1 is the volume of solvent, v_2 the volume of solute, and g is the gel fraction.

The results of the measurements are presented in Table II where the values calculated from the amount of crosslinker are listed for comparison.

They were obtained from the moles/gram data in Table I of the previous report by multiplying by the density, $\rho = 1.18$.

The χ_1 data for the two solvents were taken from the literature.[6] The difference between the two sets of values obtained in the two solvents is probably due to the inherent difficulty of obtaining reliable estimates of the interaction parameter. The crosslink densities determined in this way are from 1.5 to 5 times higher than those calculated from the amount of crosslinker assuming 100% efficiency. Calculation of the crosslink densities from preliminary stress-strain data for two samples supported the higher values.

Table II

SWELLING MEASUREMENTS ON CROSSLINKED PMMA

Lot No.	Cross-linker	Amount of Crosslinker % w/w	Gel Fraction from Swelling		Moles of Network Chains per cc x 10^4		
					From Swelling		From Amount of Crosslinker
			$(CH_2Cl)_2$	$CHCl_3$	$(CH_2Cl)_2$	$CHCl_3$	
2	EDMA	0.25	0.94	0.83	2.21	1.48	0.30
3	EDMA	1.0	0.94	0.73*	4.54	1.77	1.2
4	EDMA	6.0	0.94	0.91	9.57	7.59	7.15
5	EDMA	16.0	0.96	0.96	33.8	26.1	19.2
11	HDMA	1.0	0.90	0.91	3.07	2.59	0.93
12	HDMA	6.0	0.95	0.95	17.1	13.3	5.55

*Lot 3 was refluxed for about 24 hours in n-butyl acetate, compared with one hour for all other samples.

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