

Gradient Polymers by Diffusion Polymerization

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Synopsis

Gradient polymers are multicomponent polymers whose structures or compositions are not macroscopically homogeneous, but vary as a function of position in the sample. One method to prepare such polymers is by diffusing a guest monomer into a host polymer and then polymerizing the monomer in position to retain the concentration gradient created by the diffusion. One series of such type of materials was prepared by diffusing acrylonitrile into polystyrene. The gradient profile was determined by analyzing the nitrogen content in succeeding layers of the sample. These gradient polymers exhibit improved resistance to hydrocarbon solvents. The second series of gradient polymers was made by diffusion of methyl acrylate into poly(methyl methacrylate). These materials are shown to possess substantially increased fracture strain. Eyring's stress-biased activated rate theory of yielding was used to rationalize the observed toughening effect in gradient polymers.

INTRODUCTION

Multicomponent polymers can be produced in which the structure or composition of the polymer is not homogeneous throughout the material but varies as a function of position. In other words, these polymers have gradients in their structures or compositions, and hence may be called gradient polymers. An extreme example of gradient polymers is a layered or laminated material, where the gradient is a discontinuous step change. Other more gradual or continuous gradient profiles can be easily envisioned, e.g., linear, sigmoidal, or parabolic gradients. One potential advantage of these more gradual gradients is improved structural integrity in that delamination, often encountered in layered materials, may be avoided.

The basic concept for this type of materials has already been discussed in a previous publication.¹ In this work, we shall demonstrate the feasibility of producing these materials, and explore some of their properties. Specifically, we shall prepare gradient polymers by diffusing a guest monomer into a host polymer for a period of time just sufficient to establish a diffusion gradient profile. The monomer is then polymerized at a rate that is rapid in comparison with the rate of diffusion, so that the composition of the resultant two-component polymer varies as the diffusion gradient. Previously, Sperling^{2,3} and co-workers prepared interpenetrating networks (IPN) by swelling the host polymer in a guest monomer to equilibrium and then polymerizing the

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monomer. Thus, IPN may be considered a special case of gradient polymer in which the gradient is a flat one. In preparing gradient polymers, it is necessary to restrict host polymers to those possessing low diffusion coefficients for the monomers in order to maintain the gradient while polymerization takes place. Thus, generally, only glassy or semicrystalline polymers can be used, as the rates of diffusion of liquids through rubbers are usually much too rapid for this purpose.

Properties to be examined of the gradient polymers prepared in this work are the mechanical properties. In addition to their stress-strain behavior, the role of the presence of swelling liquids on the mechanical relaxation will also be investigated.

EXPERIMENTAL

Monomers of acrylonitrile, methyl acrylate, methyl methacrylate, ethylene dimethacrylate, and styrene were purchased from the Haven Chemical Company. Crosslinked homopolymers of styrene and methyl methacrylate were prepared by mixing the respective monomers with 1.2% by volume of the crosslinking agent (ethylene dimethacrylate). Benzoin isobutyl ether, 1.5 vol-%, (Stauffer Chemical Co.) was used as the photosensitizer. The mixture, after thorough stirring, was poured in a container with two parallel Pyrex plate glasses and polymerized by ultraviolet radiation for two days. The polymer in the form of a sheet was stored in a vacuum oven at 60°C for at least one week prior to use in order to remove remaining monomers. Random copolymers of methyl acrylate and methyl methacrylate were similarly prepared by premixing the comonomers prior to photopolymerization.

Two series of gradient polymers were prepared from these homopolymers. Polystyrene (PS) with a gradient of acrylonitrile (AN) was obtained by immersing the homopolymer in acrylonitrile monomer containing the same proportions of crosslinking agent and photosensitizer as above. The monomer mixture was allowed to diffuse into the polymer for several days at 50°C, at which temperature no decomposition of acrylonitrile is expected. The length of the immersion period, of course, determines the amount of acrylonitrile uptake. After this period, the sample was removed, quickly surface dried, and then placed in front of the UV sources for two days.

To establish the gradient profile of this gradient polymer, which we shall designate as PS/grad AN, a thick (0.5 cm) sheet of the sample was machined off layer by layer. Shavings from each layer were subsequently analyzed for nitrogen content by combustion. From the results of the combustion analysis, acrylonitrile content at each layer was calculated.

For the sake of comparison with the gradient polymers, two samples of layered structure were also made. These samples are polystyrene sheets "sandwiched" by two layers of polyacrylonitrile, and are designated as PAN/PS/PAN. They were prepared by coating a sheet of PS by hot solutions of polyacrylonitrile (Polysciences) in dimethylformamide, in which were also dissolved monomers of AN, the crosslinking agent ethylene dimethacrylate, and the photosensitizer benzoin isobutyl ether. The dissolved PAN renders the solution more viscous for easy coating on PS. The coated samples were then placed in front of UV light for two days in order for the monomer mix-

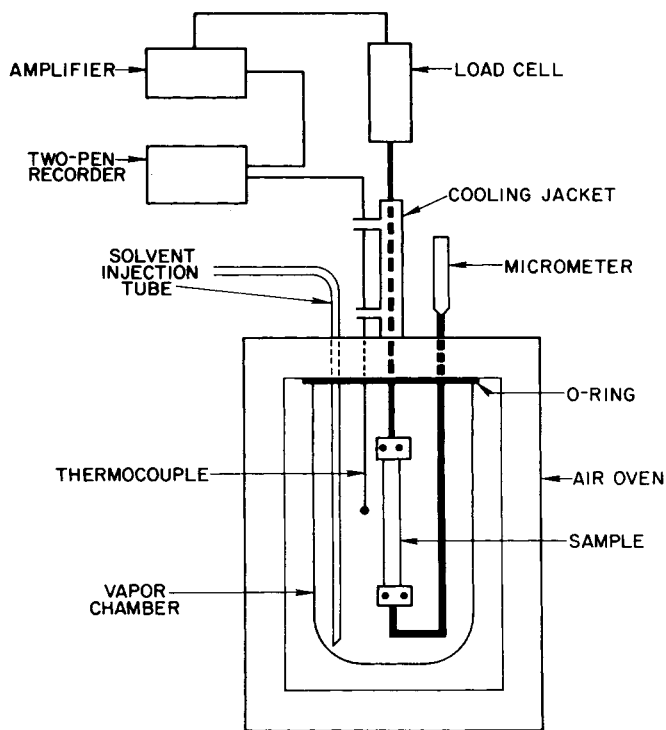


Fig. 1. Schematic diagram of the stress-relaxometer in the controlled environment of solvent vapor.

ture to form an insoluble polymer network. After removal from the polymerization chamber, the samples were subsequently dried in vacuo at 40°C for two weeks. Two samples with PAN layers of thicknesses of 0.01 and 0.025 cm were made for subsequent stress relaxation experiments. Interpenetrating networks of methyl acrylate in poly(methyl methacrylate) were made by delaying the polymerization after immersing in the monomer to allow an even distribution to establish itself. No gradient profile analysis was made for this gradient polymer, as the combustion method is not sufficiently accurate to distinguish the differences between MA and MMA, both of which contain the same elements.

Stress-strain experiments were carried out on an Instron Universal Testing Machine Model TM-SM equipped with a temperature chamber. The temperature in the chamber was controlled by a Missimers PITC temperature controller to $\pm 0.5^{\circ}\text{C}$. Samples for these measurements are approximately $0.1 \times 1.0 \times 2.0 \text{ cm}^3$.

To determine the stress relaxation behavior of the gradient polymer in the presence of solvent, a tensile stress-relaxometer was constructed and housed in an environmental chamber (Fig. 1). The sample ($\sim 0.1 \times 1.0 \times 2.0 \text{ cm}^3$) is held between two clamps. Strain is applied through the lower clamp by a micrometer. The upper clamp is connected to a Statham UL4 load cell coupled with a UC2 transducing cell. Signal for the stress is amplified by a Daytronic Model 300C Transducer Amplifier-Indicator. The rod connecting the upper clamp to the load cell is cooled by circulating water in order to minimize heat-

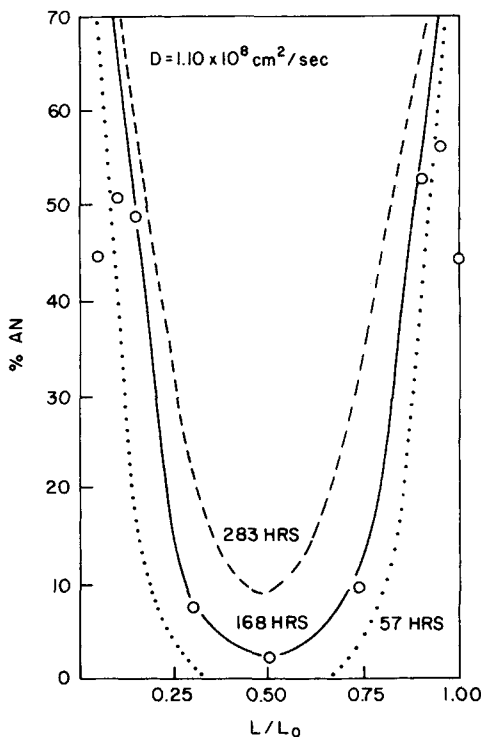


Fig. 2. Gradient profile of PS/Grad AN prepared by immersing a polystyrene crosslinked sheet in acrylonitrile monomer at 50°C. Open circles were experimental data determined by combustion analysis. Curves were computed by Fick's equation, using a diffusion coefficient of $1.10 \times 10^8 \text{ cm}^2/\text{sec}$ for immersion times of 57, 158, and 283 hr respectively.

ing of the load cell by the oven and to prevent the organic vapor from reaching the cell. To start the experiment, the sample is first deformed in the absence of solvent at the desired temperature. Temperature is monitored by a Chromel-Alumel thermocouple. The solvent reservoir is simultaneously heated to the same temperature. When the stress has been relaxed to a constant level, solvent (in this case benzene) is introduced, and stress relaxation thus initiated should be due to the effect of the diffusion of solvent into the sample. An excess of solvent is introduced into the vapor chamber in order to maintain saturated vapor pressure at the given temperature.

RESULTS AND DISCUSSION

Results from combustion analysis for a crosslinked polystyrene sheet that was immersed in acrylonitrile at 50°C for 168 hr and subsequently UV polymerized are shown in Figure 2 as open circles. Also given in the figure are curves computed by Fick's law with a constant diffusion coefficient.⁴ By choosing a curve that "best fits" the experimental data, an apparent diffusion constant of $D = 1.10 \times 10^{-8} \text{ cm}^2/\text{sec}$ was obtained. This value is, however, nearly an order of magnitude lower than that separately determined by weight uptake measurements ($D = 9.30 \times 10^{-8} \text{ cm}^2/\text{sec}$).

Another discrepancy between the computed profile and the experimental

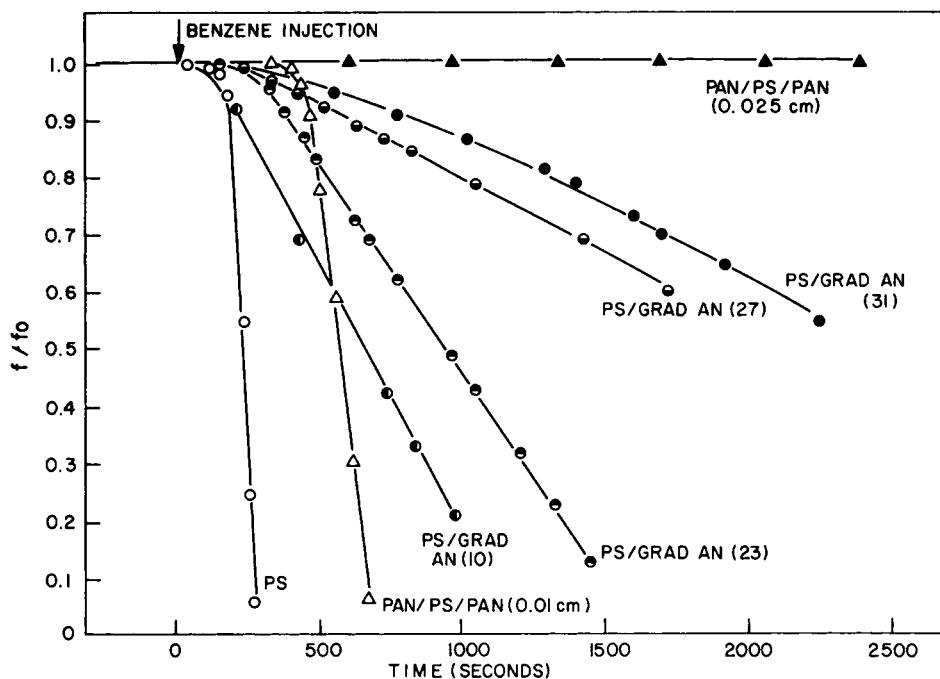


Fig. 3. Decay of elastic force due to benzene vapor for polystyrene, gradient polymers of styrene with acrylonitrile (total acrylonitrile content given in parentheses), and polystyrene "sandwiched" in layers of polyacrylonitrile (PAN) (layer thickness indicated in parentheses).

one is the acrylonitrile content near the surfaces of the sheet. The highest AN content in the gradient polymer is around 50% and is, in fact, lower in regions very near the surfaces. This observation is not surprising in view of the fact that the solubility parameter⁵ for polystyrene is in the region of 8.6–9.7 (cal/cc)^{1/2}, and that for acrylonitrile is 11.9 (cal/cc)^{1/2}. Thus, very large swelling of PS by AN is not expected. In addition, evaporation losses of AN from PS surfaces during the transfer of the polymer from monomer bath to polymerization chamber can further reduce the AN content in the surface layers of the gradient polymer.

The assumption of Fick's law for the diffusion of AN into glassy PS is also of questionable validity. It is well known that diffusion of small molecules through glassy polymers generally follows the so-called "case II" transport behavior,⁶ in which there is a superposition of relaxation-controlled transport and Fickian diffusion. Thus, the computed curves in Figure 2 can only be regarded as a crude guide for the preparation of gradient polymers. Nevertheless, the experimental data clearly establish the gradient nature of the material.

In the electron-microscopic studies by Matsuo et al.,⁷ interpenetrating network polymers have been shown to be heterogeneous. In view of the very large solubility parameter differences between PS and PAN, one can certainly expect similar microphase separation to take place. Thus, structurally one can regard the gradient polymer as layers of IPN's with domains of PS and PAN interspersed among each other, whose relative concentrations will vary continuously as a function of distance from the center of the sample outward.

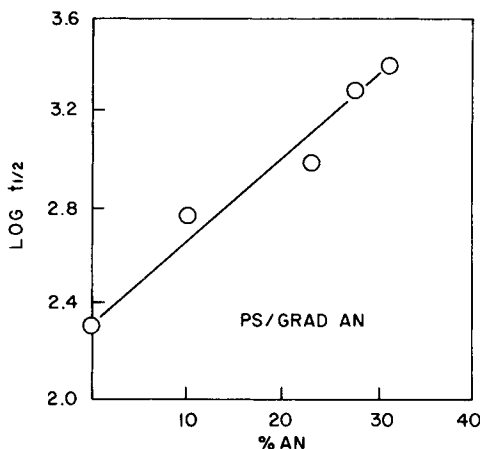


Fig. 4. Semilogarithmic plot of the times required for elastic forces of the gradient polymers of polystyrene with acrylonitrile to decay to one half of the value prior to benzene introduction as a function of total acrylonitrile content.

One interesting property that merits investigation is the solvent resistance of PS/grad AN. Polystyrene, being lyophilic, is very sensitive to the attack of hydrocarbon solvents such as benzene, whose solubility parameter is $9.2 \text{ (cal/cc)}^{1/2}$. The transmission rate⁵ (Q) of benzene through PS is $1.9 \times 10^4 \text{ g-mil/m}^2\text{-day}$. That for benzene through PAN is only $4.6 \text{ g-mil/m}^2\text{-day}$, nearly four orders of magnitude lower. Thus, one might expect that the gradient polymer PS/grad AN should show better solvent resistance than pure PS.

In Figure 3, we show the ratio of the elastic force at the moment of solvent injection (f_0) and the force as a function of time of exposure to the solvent (f). Note that the diffusion-controlled stress relaxation of PS in the presence of benzene is extremely rapid at room temperature. The stress has decayed to practically nil in less than 300 sec after benzene has been injected into the vapor chamber of our stress-relaxometer (Fig. 1). The gradient polymers, on the other hand, all exhibit improved solvent resistance with increasing total AN content. If one defines $t_{1/2}$ as the time required for the stress to relax to one half of its original value, this quantity is seen to exhibit a linear dependence on AN content in a semilogarithmic plot (Fig. 4).

For the sake of comparison, we include in Figure 3 the relaxation data for samples of three-layered PAN/PS/PAN. The sample of PS sandwiched by two layers of 0.01-cm-thick PAN showed some improvement in solvent resistance. Thicker layers of PAN (0.025 cm), however, seem to suppress the relaxation completely up to 2500 sec. It is of interest to note that even though in gradient polymers the AN content is not more than 50%, significant improvement in solvent resistance is already achievable. One potential application for these materials is for the construction of plastic gasoline tanks.⁸

The other property of gradient polymer that we have investigated is the stress-strain behavior. For this purpose, we have used our second series of gradient polymers, i.e., PMMA/grad MA. Figure 5 shows that pure PMMA at 100°C , tested at the strain rate of 0.03 sec^{-1} , is fractured around 2% strain. The gradient polymer containing 10.3% methyl acrylate now exhibits a yield point near 5% strain, and fractures above 10%. The initial moduli of the two

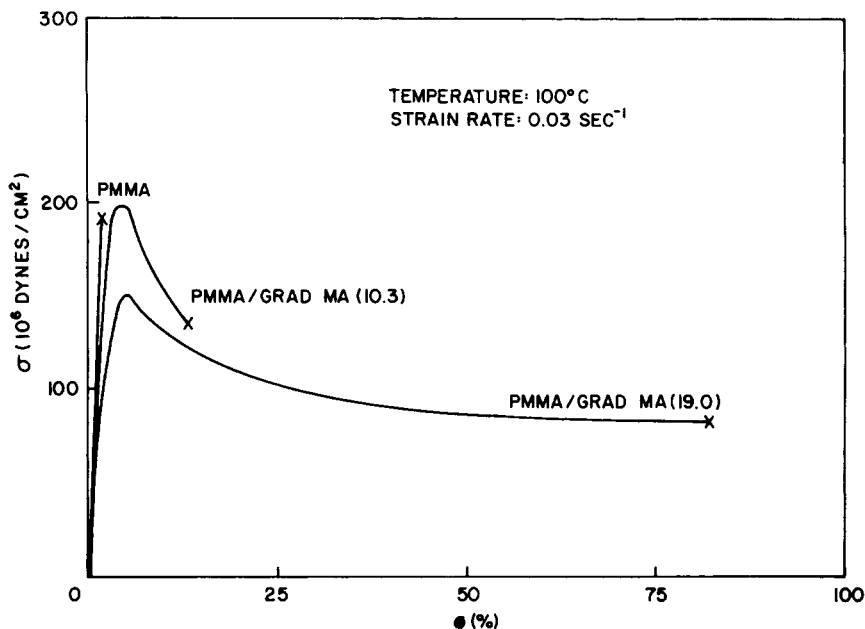


Fig. 5. Stress-strain curves of poly(methyl methacrylate) and gradient polymers of poly(methyl methacrylate) with methyl acrylate (total methyl acrylate contents are given in parentheses).

samples are very similar. In addition, the yield stress of PMMA/grad MA (10.3) is about equal to the fracture stress of the pure PMMA. Incorporation of 19% MA increased the fracture strain of the sample to almost 80% strain. The yield strain remains near that of the 10.3% gradient polymer, although the yield stress and the initial modulus have both decreased. Thus, the introduction of MA gradients into PMMA has a toughening effect on the material.

It should be pointed out that, previously, Schrenk and Alfrey⁹ showed that a three-layer polyethylene-polystyrene-polyethylene coextruded film exhibits a yield point and did not fracture up to 75% strain. The 125-layer films consisting of alternating PS and PE layers, however, fractured at less than 10% strain. All of these films are 1 mil thick, whereas our gradient samples are of the order of 30–50 mils thick.

Recently, Matsuo and co-workers⁷ have shown that moduli of IPN's vary with composition according to the Takayanagi series-parallel model. In other words, if IPN's consist of one hard and one soft component, then the modulus of the IPN is intermediate between the pure polymers. It is our view that gradient polymers consist of infinite layers of IPN's whose composition vary as a function of position. When the gradient polymer is deformed, its macroscopic strain is the same throughout the sample. Since the compositions of the layers are not the same, the harder layers must, therefore, bear greater stresses because of their higher moduli. Now, according to the Eyring's stress-biased activated rate theory of yielding,¹⁰⁻¹² the effect of applied stress is to reduce the height of the barrier for a molecular segment to jump in the forward direction and to increase it for the reverse direction. Thus, those layers in the gradient polymer having higher moduli (bearing higher stresses)

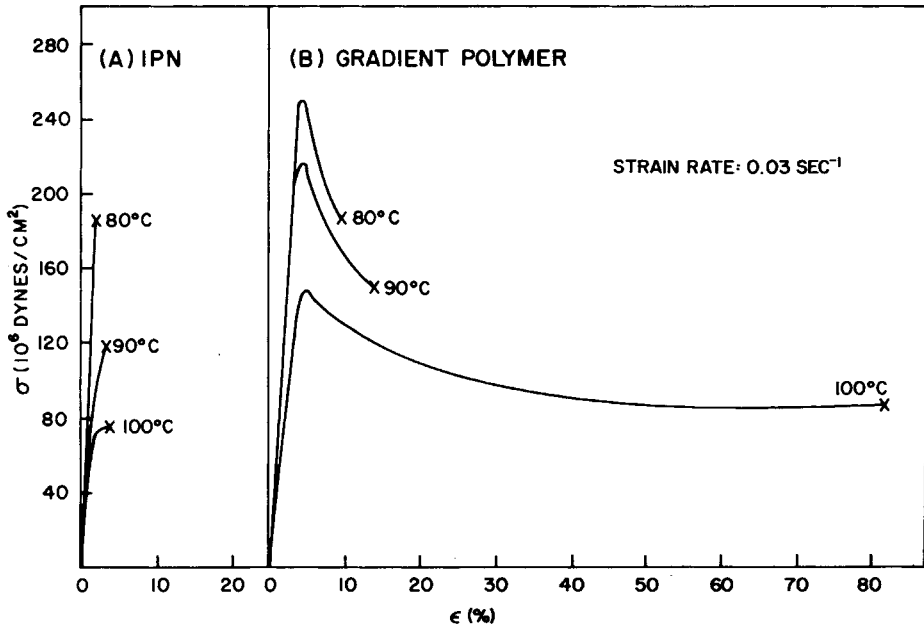


Fig. 6. Stress-strain curves of interpenetrating networks and gradient polymers at various temperatures. Total methyl acrylate contents in poly(methyl methacrylate) are 20% in both samples.

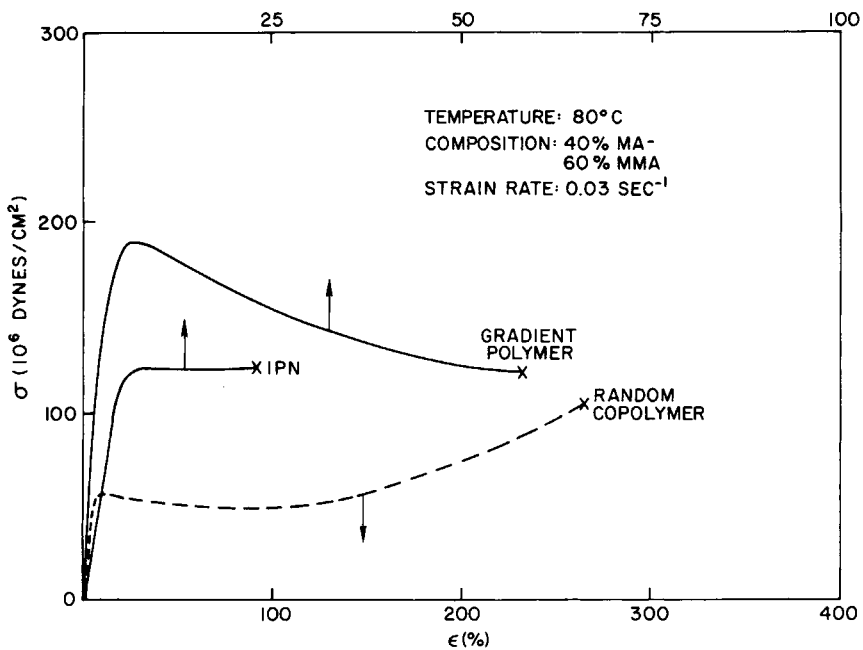


Fig. 7. Stress-strain curves of gradient polymer, interpenetrating networks, and random copolymer of methyl methacrylate and methyl acrylate (ratio 60/40).

must suffer greater stress biases than those having lower moduli. There is thus something akin to an automatic redistribution of stresses throughout the sample so that those requiring greater stress biases to flow will receive larger shares of the applied stress. The result is thus an increased yielding for the gradient polymer as a whole. A corollary to this mechanism is that it would be ineffective for polymers possessing uniform composition throughout the bulk of the sample.

An evidence which appears to be in support of this hypothesis is the comparison of the stress-strain behavior of IPN's of MMA and MA of the same composition as the gradient polymers. Figure 6 shows that at the same test temperatures and the same strain rate, IPN's do not exhibit the same toughening effect as the comparable gradient polymers. This observation is in agreement with the data of Sperling,³ who found no cold drawing or necking in IPN's. Another comparison is that with a random copolymer of the same overall composition. It is seen in Figure 7 that because the copolymer is a homogeneous material with a lower glass transition temperature, it has a low yield stress but the highest fracture strain. The IPN has a higher yield stress but lowest fracture strain. The gradient polymer has the highest yield stress and a fracture strain that is only slightly less than that of the random copolymer of comparable composition.

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