

Microscopic Domains in Some Synthetic Polymers*

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Synopsis

It was found that all pieces of poly(methyl methacrylate) have structure and anisotropy, no matter how they were made. There is no continuum, only differences of opinion about what the discontinuities represent. Judging from these and other results and pending the results of further experiments, the author is of the opinion that he has uncovered both macromolecular and micellar domains in poly(methyl methacrylate).

Regardless of wishes or expectations, a consolidated polymer is not always a homogeneous continuum. Starting in 1949,¹ if not before, it has been shown electron microscopically that a polymer may manifest various discrete domains according to kind, treatment, and properties. Cold-fractured, compression-molded polyacrylonitrile, for example, had been depicted in replica as domains roughly globular in shape, varying in average diameter from about 200 to some 840 Å. The domains were related to those shown in the dried emulsion from which the consolidated specimen was molded. In a self-supporting film cast from a solution of such a polymer, however, much smaller units dominated the picture.^{2,3} The small units were calculated on the basis of the bulk density to be of the order of 100,000 in average molecular weight. This value was commensurate with that obtained by light scattering.

Since variations in electron microscopical technique were involved, it is repeated here that the fracture surfaces were replicated with gelatin which in turn was replicated with silica, but there was no shadowing with a heavy metal. On the other hand, the specimens of dried emulsion and cast film were shadowed with a heavy metal, but no replicas were involved. Evidently, particulations of the preparatory materials did not enter the picture in either case. Evidently, too, the domains shown in the fracture surface and in the dried emulsion were families of macromolecules. They were termed micelles by Eirich and Mark⁴ in 1950. The boundaries of both discrete macromolecules and micelles may be observed in various portions of an acrylic fiber,⁵ that is, at least two of the levels⁶ of macromolecular organization must be considered. Multimacromolecular units can now be explained in the light of Gillespie's recent publication.⁷

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In thermoset resins such as phenol-formaldehyde⁵ and melamine-formaldehyde,⁶ the distinction between the two levels has been even more vague. Indeed, Erath and his colleagues currently believe that the micelle itself is the fundamental unit,^{8,9} since they have not seen smaller ones. Wohnsiedler,¹⁰ however, believes that the resinographic evidence indicates that both the macromolecule and its aggregates are meshed in a complex network, that is, the domains on the first two levels of molecular organization are very intimately integrated on a third level, that of the resinous phase itself.⁶

About 1949, too, Siegel, Johnson, and Mark,¹¹ working with dilute solutions of a polymer (polystyrene) and employing the droplet system of Boyer and Heidenreich,¹² succeeded in depicting discrete, spherical particles of sizes reasonably commensurate with the average macromolecular weights which had been obtained by independent methods. Richardson,¹³ with improved techniques, has recently confirmed the quantitative method. He also investigated the optimum proportions of good and poor solvents and their relative volatility. He confirmed the present author's depiction⁶ of the change from uncoiled to coiled macromolecules (of polyacrylamide) when a mixed solvent changed (by preferential evaporation of one component) from a good to a poor solvent.

To return to the problem of demonstrating that certain particulate domains represent single macromolecules, Peck and Moore^{14,15} have done so convincingly with highly branched polyethylene of molecular weight in the millions. By preferential etching they showed that the particles were single molecules, and by pyrolysis they showed that the macromolecules grew so large because they were so highly branched.

In 1950 the Rochow brothers and their colleagues found,¹⁶ by assuming the density of a molecular domain to be that of the bulk resin, molecular weights which were reasonably commensurate with values obtained by other routes. Recently Merrill¹⁷ pointed to the conflict between the Rochows' assumption of the "dense volume" conformation and Flory's "unperturbed random walk" conformation. Gillespie's calculations⁷ indicate that in the solid state either "the degree of entanglement must be much larger than in dilute solution" or "the individual molecules contract considerably." He also emphasizes that while polymer molecules are described in terms of an average conformation, there is probably considerable deviation from the average. Then one might expect more than one molecule to occupy the same domain and to act as a unit in flow processes. The present author has already shown that polyacrylonitrile as a film cast from solution⁸ manifests in the electron beam domains which are in the realm of discrete macromolecules.^{2,5,6} However, in emulsion-polymerized or molded samples the units are depicted as though interlocked macromolecules.^{1,5} Moreover, as a result of fiber-making processes, in fibrous samples both levels of macromolecular organization are depicted.^{5,6}

With poly(methyl methacrylate) moldings, however, the domains pictured in 1949,¹ either in polished or fractured surface, were too large (200-

800 A. in diameter) to be those of single molecules, since a commercial polymer of this kind has an average molecular weight by classical means of about 100,000. While Newman¹⁸ has increasing hesitation in accepting the topography of the fracture surface as a reflection of the structure of the matrix, Botty shows cause for increasing confidence in displaying, for example, minute latex particles of rubber in the cold-brittle fracture surface of a polyphase (polyblend) system based on poly(methyl methacrylate).¹⁹ While the fracture at room temperature shows much evidence of plastic flow of the continuous phase and rough elongation of the discontinuous phase, the brittle fracture surface shows sharp, round boundaries which are commensurate with those shown by smearing the solvent-softened specimen or by microtoming the original piece.

Incidentally, Berry has shown for consolidated, uncracked poly(methyl methacrylate) that the "inherent flow size" is a minimum at around -20°C .²⁰ While specimens studied previously by Rochow have been at approximately this temperature, in future studies the temperature of the specimen at the time of fracture will be determined more accurately.

Recently Coulehan has concluded^{21,22} that wet* stress crazing should be a function of the amorphous phase, its molecular weight,²³ and the previous orientation of the molecules.^{5,6} Moreover, he showed that the initial portion of the stress-craze fracture surface is produced slowly and smoothly compared with the subsequent portions of the fracture surface.

Therefore, it was considered of interest to compare the various types of micromorphology obtained by wet stress crazing with those obtained by brittle fracture; this was done in the present study. The molecular weight and manner of molding were also varied.

Experimental

Unless otherwise specified, the poly(methyl methacrylate) moldings were of a commercial formulation containing a small amount of ethyl acrylate in the monomer. The test bars were $1/2$ in. wide, 5 in. long, and $1/4$ or $1/2$ in. in thickness. The specimens were broken on Coulehan's stress-crazing apparatus.²¹ Many craze cracks appeared soon after the drop of alcohol wet the surface of the specimen. One of the cracks proceeded to failure. The entire fracture surface was replicated with gelatin.¹⁹ After drying, the stripped replica was placed in an enlarger and photographed at 8-fold magnification (Figs. 1, 5, 8, 11).

Figure 1 is an enlargement of the dried replica as stripped from an alcohol-wet, stress-crazed fracture surface of a compression molding of pellets of a commercial poly(methyl methacrylate). Area *A* in the upper left corner shows the smooth "eye" of the fracture which slowly developed under the drop of alcohol. As shown, the relatively smooth craze developed into concentric waves of alternately smooth and rough surfaces. The relative

* The specimen was wet with ethyl alcohol rather than with a solvent like benzene in the manner of Newman and Wolock^{23,24} or with solvent vapor in the manner of Spurr and Niegisch.²⁵

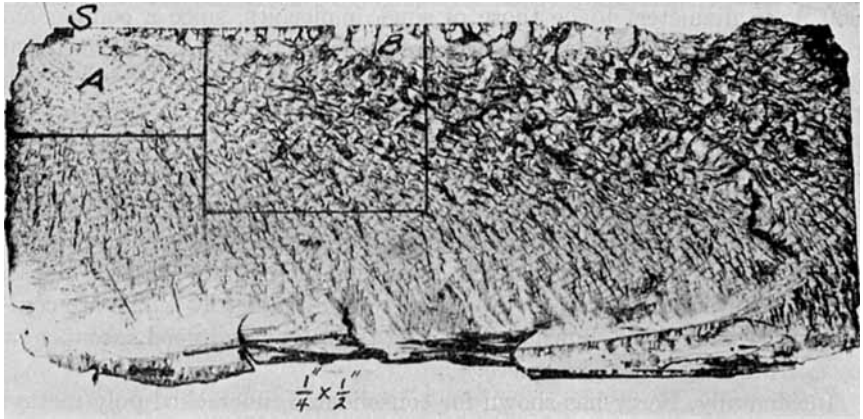


Fig. 1. Direct enlargement of primary replica of entire $\frac{1}{4} \times \frac{1}{2}$ -inch cross-section obtained by alcohol-wet, stress-craze fracture of a 5-inch test bar of compression-molded PMMA. (S) surface and location of the drop of alcohol.

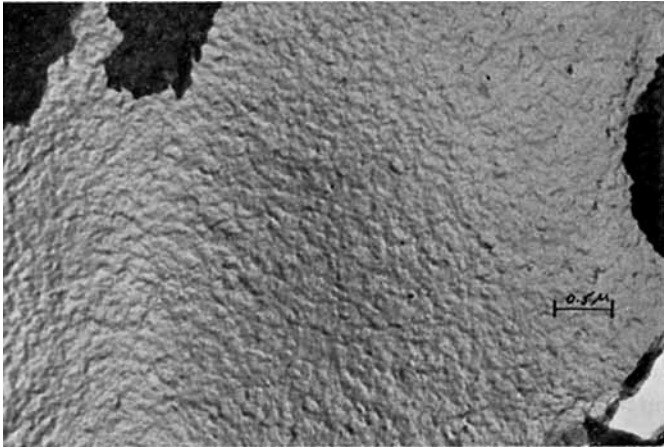


Fig. 2. Electron micrograph of secondary replica of a small portion of Area A, Figure 1. Relatively smooth surface in beginning of fracture of compression molding.

smoothness of area A compared with area B in Figure 1 is interpreted to be characteristic of the relative slowness of the initial craze-fracture.

Figure 2 is of area A and shows micelles which are commensurate with those seen before¹ in the cold-brittle fracture of compression-molded, granular poly(methyl methacrylate). Figure 3 is of area B; however, it manifests many particles in the neighborhood of 80 Å in diameter, commensurate with a molecular weight of 100,000. This is about the average molecular weight by intrinsic viscosity of a dilute solution of commercial poly(methyl methacrylate). Figure 4 is a relative blank, since it is a positive electron micrograph of a silica replica of the air-dried surface of gelatin cast upon a glass plate. Figure 4 then represents the maximum particulation introduced by the gelatin and silica replicating media and by

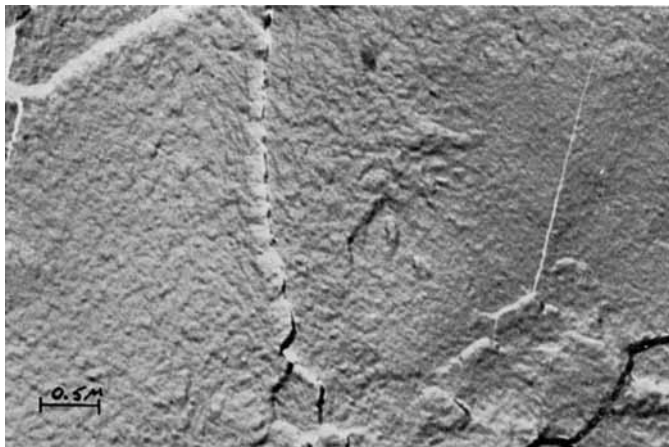


Fig. 3. Comparable, electron micrograph representing a small portion of Area B, Figure 1. More irregular surface in later (faster) fracture but fine structure much as in Figure 2.

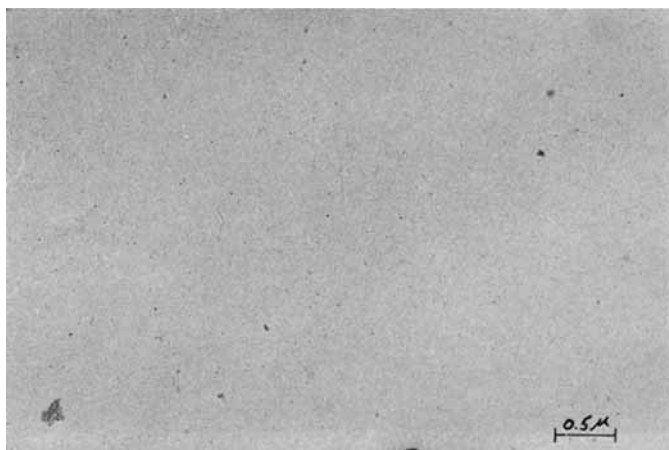


Fig. 4. Blank: Secondary replica of air-dried surface of the primary replica of surface of ordinary glass. Comparable electron micrography.

the negative and positive photographic materials under standardized exposure, development, and fixation. While there are some domains in the order of 40–80 Å.; they are very flat compared with the small domains in Figure 3. Therefore, it is concluded that the technical media hardly interfere with the perception of the macromolecular domains and not at all with the perception of micelles.

Figures 5, 6, and 7 show an alcohol-wet stress-crazed, fracture surface of an injection molding of commercial pellets of poly(methyl methacrylate) and are to be compared with Figures 1, 2, and 3, respectively. The injection-molded piece had been fractured across the direction of flow during injection. Grossly the fracture is relatively smooth (Fig. 5), but in area A

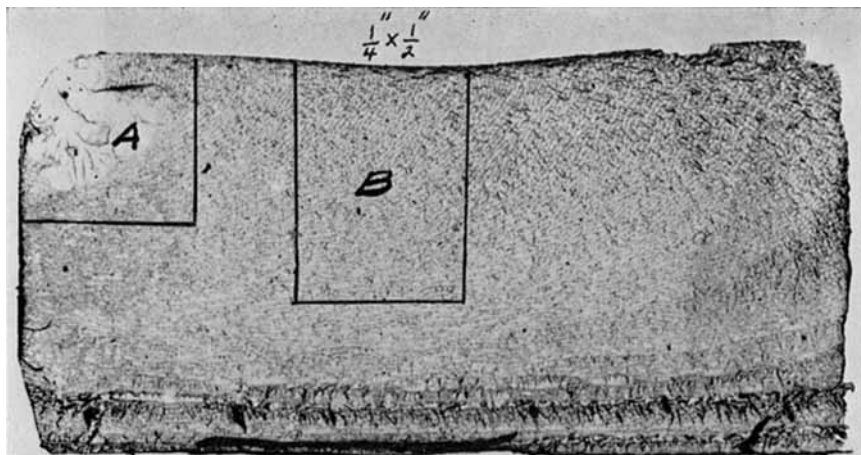


Fig. 5. Direct enlargement of alcohol-wet, stress-craze fracture of injection-molded PMMA. To be compared with Figures 1, 8, and 11.

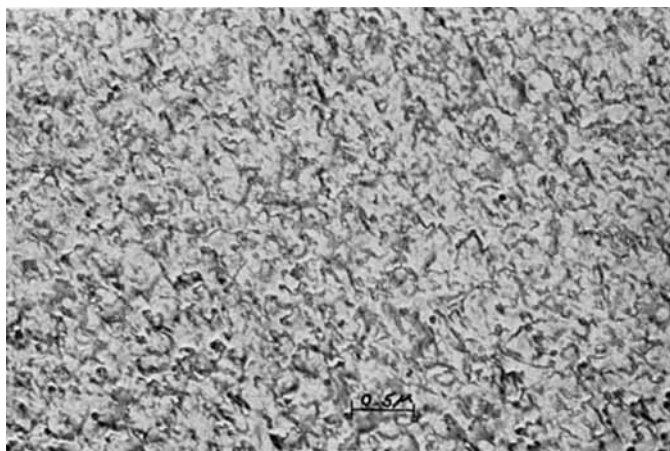


Fig. 6. Electron micrograph of small portion of Area A, Figure 5, of injection molding. Effect of injection flow is manifest. To be compared with Figures 2, 9, and 12.

(Fig. 6) the crosswise effect of flow is manifest in the fracture surface. In Figure 7, however, the wave effect during fracture dominates. The result is an alternation between a micellar texture (shown in upper portion, Fig. 7) and a macromolecular one (lower portion, Fig. 7).

Figures 8, 9, and 10 show an alcohol-wet, stress-crazed, fracture surface of a commercially cast sheet of poly(methyl methacrylate). As shown in the upper edge of Figure 8, stress crazing took place all along the wetted face of the cast piece. Failure then proceeded in a relatively smooth area A (Fig. 9), and ultimately into an area full of parabolic figures which developed, according to Berry, by the intersection of linear and circular crack fronts.²⁶ The microtextures of the fractured casting as shown in Figures 9 and 10 are relatively coarse compared with those shown in the compression

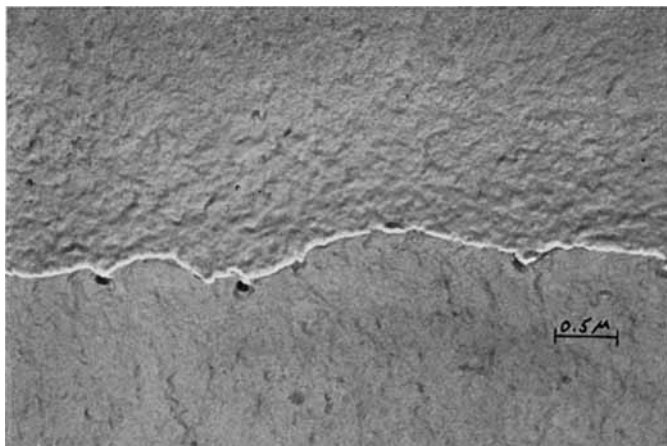


Fig. 7. Comparable, electron micrograph representing Area B, Figure 5, of injection molding. Effect of waves. To be compared with Figures 3, 10, and 13.

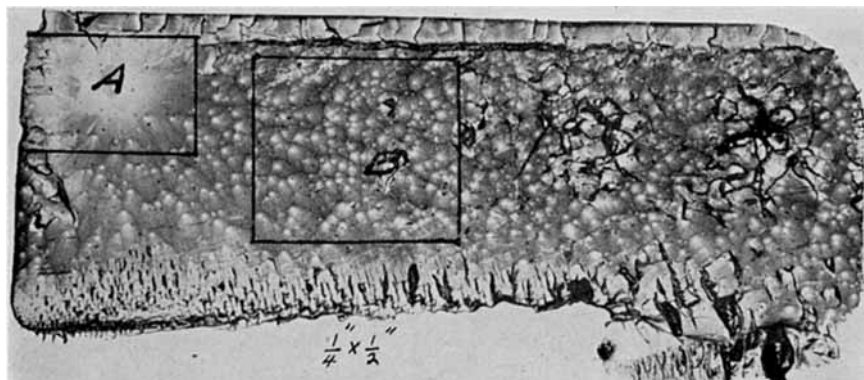


Fig. 8. Direct enlargement of alcohol-wet stress-craze fracture of commercially cast PMMA. To be compared with Figures 1, 5, and 11.



Fig. 9. Electron micrograph of small portion of Area A, Figure 8, of casting. To be compared with Figures 2, 6, and 12.

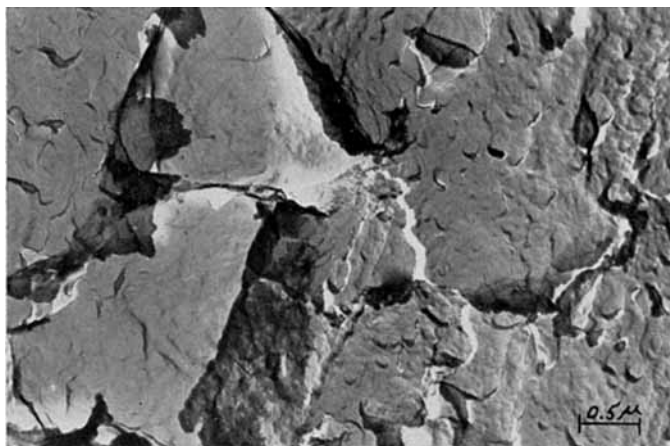


Fig. 10. Comparable electron micrograph representing Area B, Figure 8, of casting. To be compared with Figures 3, 7, and 13.

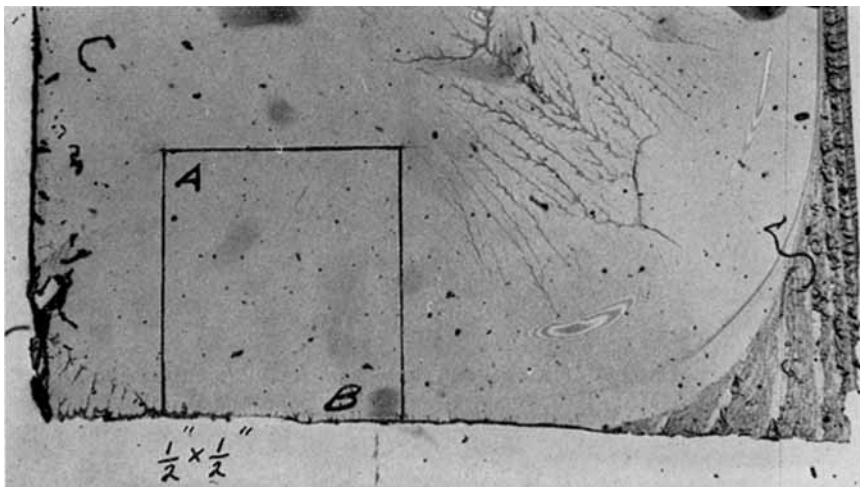


Fig. 11. Direct enlargement of alcohol wet, stress-induced but with very slow fracture of injection molding. To be compared with Figures 1, 5, and 8.

molding (Figs. 2 and 3) and injection molding (Figs. 6 and 7), but micelles are manifested in Figure 9 and (less distinctly) in Figure 10, in spite of the relatively rough fracture surface.

In his very recent experiments, Coulehan²¹ found that he could obtain an extremely smooth, glassy fracture in his apparatus, provided he reduced the stress after initial crazing²² so as to produce very slow fracturing. We found that the resulting fracture surface was unusually smooth, as shown in Figure 11. While some areas of fracture (Fig. 12) are like the upper portion of Figure 7, most of the fracture, represented by Figure 13, is more like the lower part of Figure 7. The domains shown in Figure 13 are generally

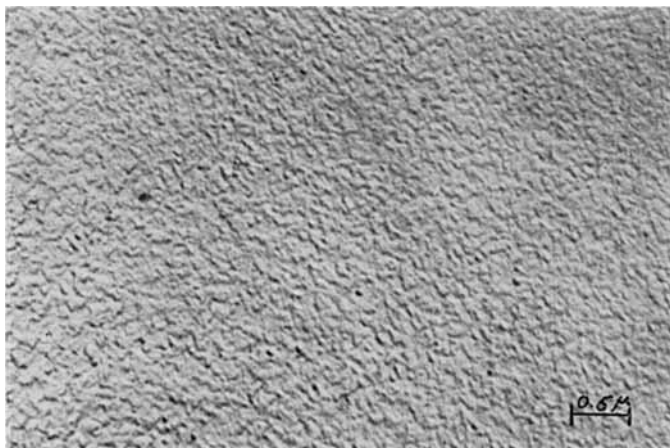


Fig. 12. Electron micrograph of small portion of Area A, Figure 11. To be compared with Figure 2, upper portion of Figure 7, and Reference 1.

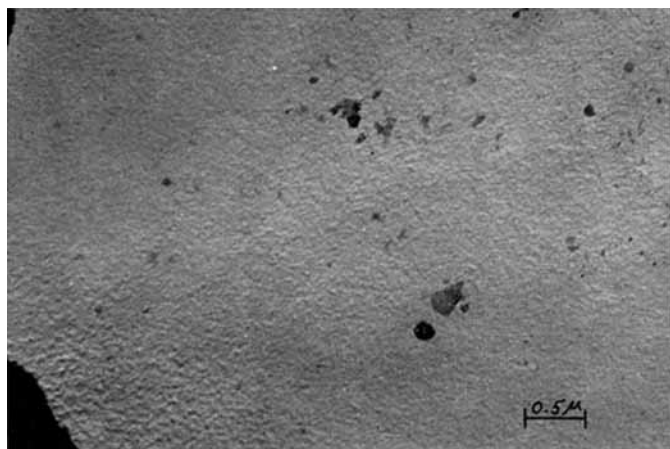


Fig. 13. Comparable electron micrograph representing Area B, Figure 11. To be compared with lower part of Figure 7, as a result of extremely slow fracturing (practically without the use of external stress).

about 80 Å across, that is, they are commensurate with spherical domains of molecular weight 100,000, the nominal average for this commercial grade of poly(methyl methacrylate). We conclude that some molecular domains have been exposed by wet-stress crazing. We also agree with Coulehan^{21,22} that such crazing is the result of disentanglement of molecular domains rather than molecular cleavage.

Larger Domains

The molding pellets or beads used in fabricating a molded plastic "re-member" their own identity. For example, in a compression-molded test bar of poly(methyl methacrylate) there was little flow of the pellets during

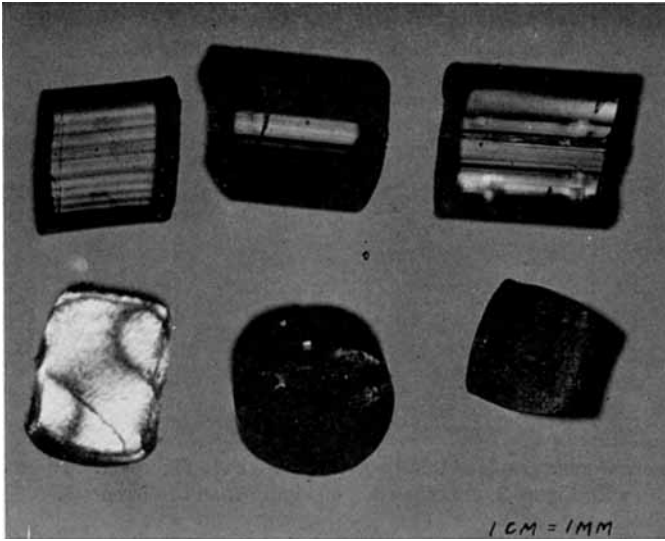


Fig. 14. Top row: Longitudinal view of pellets of various manufacturers. Bottom row: Cross-sectional view of representative pellets. All in air between crossed polars.

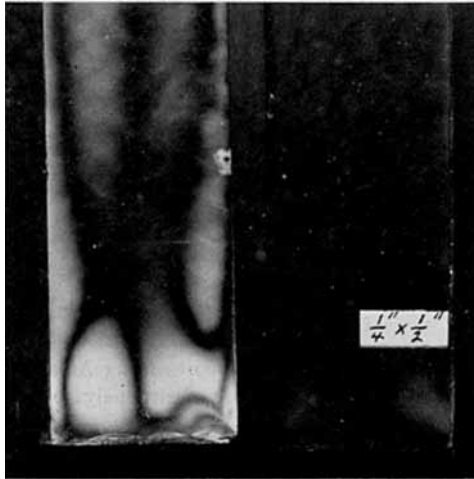


Fig. 15. Left: Compression-molded test bar, as molded, between crossed polars. Right: Comparable bar, annealed above glass temperature. Note reference 6.

the molding process, each pellet "remembering" its identity.⁶ The volume of each molding unit was apparently held intact, and its shape was plastically deformed to pack it against its neighbors. The resulting grain boundaries must mean that there is little mixing or other interaction at the surfaces of the pellets as they form interfaces during the molding process. The discrete identities must also mean that each original pellet has characteristics of its own, which perhaps include surface oxidation or an adsorbed film that hindered adhesion of surfaces during the brief period of

molding. For example, in Figure 14, the top row shows a longitudinal view of typical pellets of a commercial molding grade from three different manufacturers. In the bottom row are shown the cross-sectional views of the same types of pellets. All six pellets were photographed in air between crossed polars by transmitted light. The three pairs, while comparable, differ somewhat in shape, anisotropy, manufacture, and composition. While each manufacturer maintains strict quality control, the strain anisotropy and variations in shape indicate directional characteristics for each individual pellet in any sample. As each individual is forced into place, it acquires a strain which it "remembers." The underlying stress may be relieved somewhat by annealing above the glass temperature (Fig. 15), but as seen before,⁶ reticulation of the surface results.

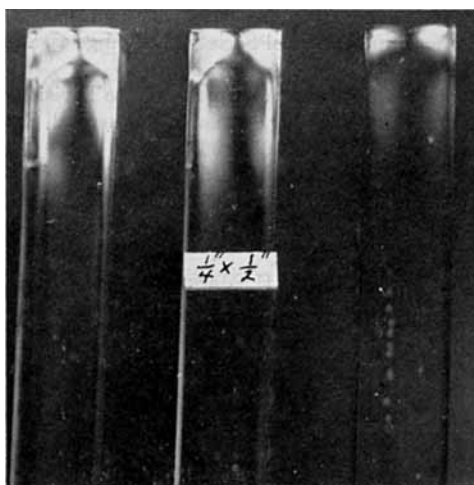


Fig. 16. Injection molded test bars between crossed polars. Molded bars are in same order as in Figure 14 with respect to anisotropy and to manufacturer.

Anisotropy is not confined to compression or extrusion; injection-molded pieces also show anisotropy. While the identity of the individual pellets is apparently lost by injection molding, the order of difference in anisotropy among pellets of different manufacture prevails, as shown in Figure 16.

It seems, therefore, that one may not make the general statement²⁶ that glassy polymers lack structural order and that body responses can adequately be represented as those of an isotropic elastic continuum down to essentially molecular dimension.

To our knowledge this is the first time that domains as small as average macromolecules have been shown in a consolidated thermoplastic. They have been shown by evaporation of a suitable mixed solvent,¹³ so we know that monomolecular domains do exist. Generally, however, we have seen domains which are apparently aggregates (micelles⁴) of macromolecules. These aggregates originate in the molding pellets or beads.

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Résumé

On a trouvé que toutes les pièces de polyméthacrylate de méthyle possèdent une structure et une anisotropie indépendante de la manière dont elles ont été faites. Il n'y a pas de continuité mais uniquement une différence d'opinion au sujet de ce que les discontinuités représentent. D'après ces résultats et d'autres et en attendant ceux d'expériences ultérieures, les auteurs pensent qu'ils ont découvert les deux domaines macromoléculaire et micellaire dans le polyméthacrylate de méthyle.

Zusammenfassung

Es zeigte sich, dass unabhängig von der Art der Darstellung alle Stücke von Poly(methylmethacrylat) Struktur und Anisotropie besitzen. Es bildet sich kein Kontinuum, sondern nur Meinungsverschiedenheit darüber, worauf die Diskontinuitäten beruhen. Nach diesen und anderen Ergebnissen zu urteilen und in Anbetracht der Resultate weiterer Versuche ist der Autor der Ansicht, sowohl makromolekulare als auch micellare Bereiche in Poly(methylmethacrylat) aufgezeigt zu haben.

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