

Gas-Filled Polymers. III. Mechanical Behavior of Polycarbonate and Poly(vinyl Chloride)

A. G. KOLBECK, H. FUJIMOTO, and D. R. UHLMANN,
*Department of Metallurgy and Materials Science, Center for Materials
Science and Engineering, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139, and P. D. CALVERT,
School of Molecular Sciences, University of Sussex
Falmer, Brighton, England*

Synopsis

Gasification behavior and its effects on mechanical properties were determined for amorphous polycarbonate (PC) and poly(vinyl chloride) (PVC). Nitrogen-gasified PC and PVC exhibit interior regions containing gas bubbles surrounded by surface layers of void-free polymer, while in the helium-gasified polymers no gas bubbles could be observed. Scanning electron microscope (SEM) observations of the bubbles in nitrogen-gasified PC indicate that the bubble walls are smooth and featureless (in contrast to the diffuse walls with fibrils of polymer extending into the bubbles observed previously in gasified polyethylene). For both PC and PVC, neither the yield stress nor the elongation to fracture showed any appreciable variation between gasified and ungasified material. The lack of a significant effect of gas bubbles on the drawing behavior in these glassy polymers stands in contrast with the pronounced effect noted with semicrystalline polyethylene. The origin of this difference in behavior and its relation to the crystallization process in polyethylene are discussed.

INTRODUCTION

Work reported in previous papers^{1,2} has been concerned with the effects of gasification treatments on the semicrystalline polymers, high-density polyethylene, and low-density polyethylene. Attention was directed to the conditions required for the formation of gas bubbles in the polymers, to the morphologies of the bubbles, and to their effects on the mechanical properties. In the present paper, we shall report on investigation of the effects of similar gasification treatments on two essentially amorphous polymers, bisphenol A polycarbonate (PC) and poly(vinyl chloride) (PVC).

Work reported elsewhere in the literature (see summary in ref. 3) has dealt with foams based on both PVC and PC. As in the case of polyethylene foams, however, all of the attention appears to have been directed to foams with densities less than about half the densities of the bulk polymers. The present study was concerned with high-density materials, characterized by densities above 80% of those of the bulk polymers. No information appears to be available on the behavior of such materials.

EXPERIMENTAL

The polycarbonate used in the present investigation was Lexan PC, supplied by General Electric in the form of sheets 0.09 cm in thickness. Differential scanning calorimetry (DSC) at a heating rate of 10°C/min indicated a glass transition of about 150°C for the material. The poly(vinyl chloride) was an unplasticized PVC, supplied by Owens-Illinois in the form of sheets 0.09 cm in thickness. Its glass transition was indicated by the DSC method to occur at about 75°C.

Details of the gasification procedure have been described elsewhere¹ and may be briefly reviewed here. The specimens, approximately 15 cm × 3 cm, were clamped to an aluminum holder and placed inside a pressurizing cylinder. The apparatus was then heated to the desired annealing temperature under a pressure of 1500 psi of nitrogen or helium. Upon completion of the anneal, the apparatus was cooled by forced-air convection to room temperature, the pressure released, and the samples removed.

Following the pressurizing treatment, most of the specimens were given a second anneal at atmospheric pressure at temperatures of 10° to 20°C above the glass transition temperatures of the respective polymers. To minimize warping of the specimens, the procedure of cooling under gas pressure in the original gasification procedure followed by the second anneal at atmospheric pressure was employed, rather than releasing the gas pressure prior to cooling. Density measurements of gas-filled PC gave values ranging from 0.80 to 1.12 g/cm³, compared to a value of 1.19 g/cm³ for ungasified PC. Also, gasification gave no noticeable change in the glass transition temperature of either PC or PVC as determined calorimetrically.

Following the indicated heat treatments, samples were die cut into dumb-bell-shaped tensile specimens with a gauge length of 5.1 cm (ASTM D638) and subjected to mechanical tests using a table model Instron machine at a rate of 0.05 in./min for the PC and 0.02 in./min for the PVC. In order to minimize effects due to residual orientation in the sheets, all samples were cut in the same direction. All values to be reported for the yield stress and elongation to fracture are nominal, based on the original cross section and gauge length of the specimens.

RESULTS

Upon removal from the pressurizing apparatus at room temperature, all specimens were optically clear for any of the gasification treatments employed. Following the high-temperature anneal at atmospheric pressure, specimens of both PVC and PC were observed to have changed from transparent to opaque white when nitrogen was used in the original gasification treatment. The opacity was due to the formation of gas bubbles in the specimens. In contrast to this behavior, samples of both PVC and PC remained transparent after the high-temperature anneal at atmospheric pressure when helium was used in the original gasification treatment.

TABLE I
Mechanical Properties of Gasified PC^a

	Yield stress, psi	Elongation to fracture, %
Control samples, as-received (average of 3 tests)	7700 ± 300	85 ± 20
Control samples, once-annealed (heat treatment 155°C, 30 min, 1 atm; average of 4 tests)	8300 ± 300	135 ± 20
Transparent N ₂ -gasified PC (heat treatment 155°C, 30 min, 1500 psi N ₂ ; average of two tests)	8200 ± 100	90 ± 25
Opaque N ₂ -gasified PC (heat treatment 162°C, 20 min, 1500 psi N ₂ followed by 155°C, 30 min, 1 atm; average of 3 tests)	7700 ± 300	55 ± 20
Transparent He-gasified PC (heat treatment 162°C, 20 min, 1500 psi He followed by 155°C, 30 min, 1 atm; average of 3 tests)	8700 ± 400	65 ± 10

^a Strain rate 0.05 in./min.

Polycarbonate

Results of the tensile tests on PC are given in Table I. For ungasified control samples, both as-received and once-annealed, the values of the yield stress (7700–8300 psi) and elongation to fracture (75–125%) agree well with values reported in the literature.⁴ Similar agreement with other work⁵ was found for the strain at yield (7–9%, not reported in Table I).

Nitrogen-gasified PC samples, when tested prior to the secondary anneal (such that the material remained transparent), showed no appreciable differences compared to ungasified PC, with perhaps a slight reduction in elongation to fracture relative to once-annealed, ungasified PC. Gasified specimens of PC which were given the annealing treatment at atmospheric pressure were in the same range as those of the ungasified control samples. The elongation to fracture, however, showed a decrease to 54% for gasified, opaque PC from values of 85% and 135% for as-received and once-annealed, ungasified PC, respectively. No significant variation in draw ratio between as-received PC and nitrogen-gasified PC was noted, with a value of approximately 1.6 found for both materials.

The form of the stress-strain curve obtained for nitrogen-gasified PC was similar to that of the ungasified material, exhibiting a sharp yield point followed by cold-drawing at a nearly constant stress level until fracture. Yielding was invariably accompanied by the formation of a distinct neck. However, while the ungasified PC and the gasified but nonopaque PC yielded by the formation of shear bands at 45 degrees to the stress axis prior to necking, necking in the opaque nitrogen-gasified PC occurred without formation of the deformation bands. Fracture of both the gasified and ungasified material always occurred in an abrupt manner within the necked portion of the specimens.



Fig. 1. Void morphology in nitrogen-gasified PC. Heat treatment 160°C, 30 min, 1500 psi N₂, cooled to room temperature, followed by 150°C, 15 min, 1 atm. Magnification 30X. Arrow indicates surface of specimen.

All samples of helium-gasified PC whose behavior is reported in Table I remained transparent. Results of the tensile tests show an increase of 5–10% in the yield stress compared to both the control samples and the nitrogen-gasified PC. The elongation to fracture, however, showed a reduction to about half the value for ungasified, once-annealed material, similar to the reduction found for nitrogen-gasified PC. The drawing phenomena of the helium-gasified PC was similar to that of the nitrogen-gasified PC with the sharp yield point and subsequent drawing at nearly constant stress, but without shear banding being observed. The draw ratio of helium-gasified PC was found to be identical to that of the as-received material.

The morphologies of the bubbles in nitrogen-gasified PC were studied in the optical microscope at low magnification, viewing the specimen by reflected light through the thinnest dimension of the sheet (about 1 mm). Figure 1 shows a typical micrograph of the bubble structure of nitrogen-gasified PC. A void-free surface layer 0.04 cm thick is evident. The gas bubbles within the central region of the specimen are approximately spherical in shape, about 0.0025 cm in diameter, and are distinctly separated from one another.

Figure 2 shows a micrograph of the necked region of a nitrogen-gasified PC specimen after drawing in tension. The bubble morphologies are similar to those in the undrawn material (Fig. 1), save for an elongation of the bubbles in the draw direction.

To investigate the internal features of the voids in nitrogen-gasified PC, samples were examined in the scanning electron microscope (SEM). The preparation technique consisted of forming a fresh surface of the cross section of the material with a knife, coating with a thin conductive layer of gold, and viewing immediately in the SEM. Micrographs obtained on a specimen with a relatively small degree of opacity are shown in Figure 3.

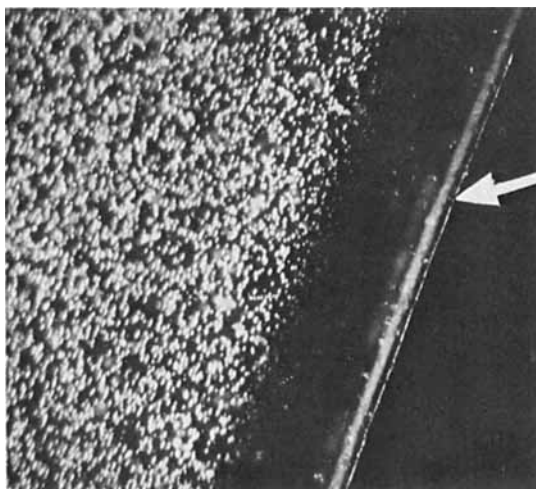


Fig. 2. Void morphology in nitrogen-gasified PC after tensile drawing. Heat treatment same as in Fig. 1. Magnification 30 \times . Arrow indicates surface of specimen. Direction of stress is parallel to specimen surface.

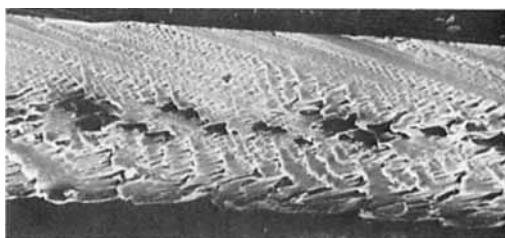
As indicated in Figure 3a, the gas bubbles at low magnification appear as dark depressions along the central plane of the specimen, and the void-free surface layers are clearly evident on either side of the row of voids. The oblique striations and the scale-like features stacked normal to the edges of the specimen are artifacts of the knife-cutting process used in forming the surface. Samples of the ungasified PC viewed under identical conditions showed no evidence of voids but appeared essentially identical to the void-free surface layers of Figure 3a.

Figure 3b shows a typical single void at high magnification. The most notable feature is the apparent lack of any internal structure. At still higher magnifications, the void walls appear smooth and featureless. This lack of internal void structure is in sharp contrast to the void morphology of gas-filled polyethylene (see discussion in ref. 1 and discussion below).

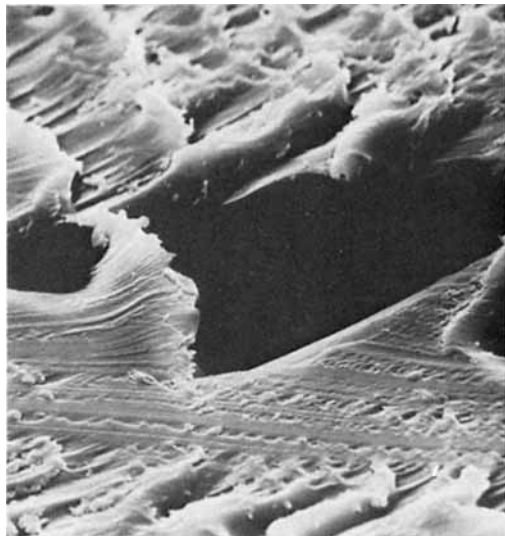
Poly(vinyl Chloride)

Table II gives the results of tensile tests on PVC. While the yield stress did not vary significantly between annealed and as-received specimens, the elongation to fracture dropped by 50% for the annealed material. The as-received samples yielded with the formation of a sharp neck, followed by propagation of the neck at a nearly constant stress level. The once-annealed material also formed sharp necks, but no propagation of these necks was observed. Rather, tear-type fractures were initiated at the neck shoulders soon after yield. These led to failure at relatively low strains.

The above results were obtained on specimens cut from the as-received PVC sheet parallel to the machine direction of the sheet. Samples formed with orientations perpendicular to this exhibited drawing behavior identical



(a)



(b)

Fig. 3. Void morphology of nitrogen-gasified PC in SEM. Magnification: (a) 60 \times ; (b) 1200 \times .

to that of once-annealed samples of the first orientation, i.e., lower elongation to fracture accompanied by tear-type fractures initiated at the boundary between necked and unnecked regions. This indicates that orientation is present in the as-received PVC. Annealing of the parallel-aligned material reduces the degree of orientation and leads to drawing behavior similar to that observed for the less oriented direction of the sheet. The results on gasified PVC were all obtained on samples cut in the more highly oriented direction.

PVC samples which had been gasified with either nitrogen or helium and subsequently annealed above T_g at atmospheric pressure show no clearcut differences for the yield stress and elongation to fracture as compared with the ungasified material. Significant effects were, however, noted in the drawing behavior, where both nitrogen-gasified and helium-gasified material drew uniformly until fracture occurred in an abrupt manner (without the formation of a sharp neck and in contrast with the tearing-type fracture observed in annealed but ungasified control samples).

TABLE II
Mechanical Properties of Gasified PVC^a

	Yield stress, psi	Elongation to fracture, %
Control samples, as-received (average of 4 tests)	7000 ± 200	22 ± 5
Control samples once-annealed (heat treatment 110°C, 20 min, 1 atm; average of 5 tests)	6900 ± 500	9 ± 3
N ₂ -gasified PVC (heat treatment 110°C, 20 min, 1500 psi N ₂ followed by 110°C, 15 min, 1 atm; average of 5 tests)	7400 ± 500	16 ± 5
He-gasified PVC (heat treatment 112°C, 20 min, 1500 psi He followed by 110°C, 15 min, 1 atm; average of 4 tests)	7100 ± 300	18 ± 3

^a Strain rate 0.02 in./min.

The draw ratios of ungasified, nitrogen-gasified, and helium-gasified PVC were all in the range of 1.5 to 2.1, with no significant variations discernible between treatments.

Specimens of opaque, nitrogen-gasified PVC were examined in the optical microscope to observe the void morphologies. Even at magnifications of 200X, however, no separate and distinct gas bubbles could be resolved (the samples appeared uniformly white). A void-free surface layer was observed around the edges of the specimen. The thickness of this layer was smaller than that found in nitrogen-gasified PC (0.005–0.010 cm in PVC compared with 0.04 cm in PC).

SEM studies of nitrogen-gasified PVC also gave no indication of a distinct void structure even at magnifications greater than 1000X. The surface appeared rough and textured to an extent similar to that found in specimens of ungasified PVC studied by the same technique. It appears likely that the voids occur on a scale fine enough to be completely hidden by the sample preparation technique.

DISCUSSION

To facilitate comparison of the present data with those on gas-filled polyethylene,^{1,2} the pertinent results of the PE studies will be briefly recapitulated. With both high-density and low-density PE, at least partial melting of the crystalline component was required for the formation of observable gas bubbles.¹ The bubbles, when formed, were generally characterized by elongated shapes, with their long dimensions often oriented parallel to the surfaces of the specimens. A bubble-free surface layer was invariably noted. Nitrogen-gasified and helium-gasified PE showed different gas bubble morphologies, with nitrogen gasification resulting in many more but smaller bubbles than helium gasification. The presence of gas bubbles in PE led to a slight reduction of the yield stress and an order of magnitude decrease in the elongation to fracture, with the normal cold-

drawing behavior of ungasified PE being eliminated by gasification. Optical microscopy showed that the decreases in mechanical properties, particularly the elongation to fracture, could be directly related to the presence of gas bubbles. Drawing gasified PE was accompanied by growth of the gas bubbles until the remaining unfractured polymer between bubbles was insufficient to support the applied load.

The first distinction between gasified PC and PVC and gasified PE involves the formation of gas bubbles. With PE, the melting region proved to be the critical temperature range below which bubble formation was not observed, while with the two amorphous polymers the region of the glass transition was critical. With PVC no bubble formation was noted for gasification below 85°C, 10°C above T_g , as measured by scanning calorimetry. Even for gasification at 105°C, a secondary, atmospheric pressure anneal at 70°C for as long as 24 hr gave no indication of gas bubble formation, while subsequent annealing of the same sample of 100°C led to whitening within 30 min. With nitrogen-gasified PC, 150°C was the lowest temperature for which gas bubbles could be observed—again the region of the glass transition. The correlation of bubble formation with the melting range for semicrystalline polymers and with the glass transition region for amorphous polymers apparently reflects the respective temperature ranges where chain mobility becomes significant. This mobility allows rapid access of the diffusing gas to the interior of the polymer and gives rise to sufficient supersaturations for bubble formation upon crystallization of the PE and upon reannealing the PC and PVC at atmospheric pressure. Significant chain mobility also appears to be required for diffusion of the dissolved gas at atmospheric pressure to nucleated bubbles. The void-free surface layers indicate the effectiveness of the surfaces as sinks for dissolved gas.

A second difference between the gasification behavior of PC and PVC as compared with PE concerns the effect of helium. While all three polymers formed bubbles with nitrogen gasification, only PE could be induced to form gas bubbles with helium. Even in the case of PE, however, bubble formation was greatly reduced for helium relative to nitrogen. These differences can be related to differences in the diffusion coefficients and solubilities of helium and nitrogen in the polymers. The diffusion coefficient of helium in PE is an order of magnitude larger than that of nitrogen,⁶ and a tabulation of diffusion coefficients of gases in polymers⁷ indicates a much higher diffusion coefficient for helium relative to nitrogen wherever they could be directly compared (but not specifically for PC and PVC).

On the basis of correlations given by Van Krevelen,⁸ it is possible to estimate these diffusion coefficients and solubilities at any temperature. The calculated values are given in Table III and can be taken as representative of the relative magnitudes of these parameters. The equilibrium concentration (C) of dissolved gas in the polymer can be related to the solubility (S) by Henry's law:

$$C = S \cdot p$$

TABLE III
Solubilities and Diffusivities of Nitrogen and Helium in PC and PVC, Estimated from Correlations of Ref 8

Polymer	Gas	Temp., °C	Diffusivity D , cm ² /sec	Solubility, S , cm ³ (S.T.P.)/cm ³ polymer · atm
PVC	N ₂	27	6×10^{-8}	
PVC	N ₂	110	9×10^{-6}	6×10^{-2}
PVC	He	27	3×10^{-6}	
PVC	He	110	3×10^{-5}	10^{-4}
PC	N ₂	27	3×10^{-7}	
PC	N ₂	155	8×10^{-5}	6×10^{-2}
PC	He	27	7×10^{-6}	
PC	He	155	9×10^{-5}	2×10^{-4}

where p is the partial pressure of the gas. The diffusion coefficient for nitrogen in PVC is an order of magnitude lower than that in PC at the annealing temperature. This correlates with the appearance of smaller, more numerous bubbles and a thinner, bubble-free surface layer in PVC. The observed widths of the bubble-free layers are in agreement with values calculated for a random walk diffusion of gas to the surface at room temperature over a time of 10^3 sec. This might suggest that the surface layers result from gas loss before the annealing treatment rather than concurrently with bubble formation during annealing. It was observed experimentally, however, that surface layers of similar extent were formed in samples which had been held at room temperature prior to the atmospheric pressure anneal for periods ranging from minutes to days. This seems to indicate that the loss of gas through the surface at high temperatures is dominant and perhaps that the diffusion coefficients estimated from reference 8 for room temperature may be somewhat high.

From Table III, the estimated solubilities indicate that the lack of bubble formation after helium gasification is primarily due to the low solubility of this gas in the polymers. In view of the uncertain reliability of the correlations, however, this conclusion can be regarded as only tentative.

The difference in the effects of helium gasification between semicrystalline PE and amorphous PC and PVC is likely due to a large supersaturation arising during the crystallisation of the PE. For the two amorphous polymers, the solubility of helium is apparently low enough to keep the degree of supersaturation below that required for bubble nucleation. In the case of PE, the rejection of dissolved gas at the advancing crystal-liquid interfaces can result in a supersaturation which is locally high and apparently sufficient for nucleation.

In addition to differences in the response of these polymers to helium gasification, the morphologies of the gas bubbles produced by nitrogen treatment are also different. In PE, the bubbles are elongated in shape and the boundaries between gas and polymer are rough and composed of fibrils of polymer extending into the bubbles.¹ In PC, the bubbles are nearly

spherical and the boundaries are smooth and featureless. In PVC, no distinct gas bubbles can be discerned in the optical microscope. The morphological difference between PE and PC seems understandable: in PE, the bubble formation appears to be controlled by crystallization and the morphology of the voids must be accommodated to the crystals; while in PC the minimization of surface energy would be expected to result in spherical bubbles.

The differences in internal structure of the gas bubbles can also be explained in terms of structural differences between the polymers. The presence of the crystalline phase in PE should influence the structure of the gas-polymer interface both because the crystalline material may provide more resistance to the internal pressure of the growing bubbles and, more significantly, because the amorphous regions, with their higher concentrations of dissolved gas, offer a richer source of gas to the growing bubbles. In PC, no crystalline phase with properties different from the amorphous material intervenes, and the formation of gas bubbles can more adequately be considered as the growth of bubbles in a homogeneous medium. In this case, surface energy effects would not be dominated by variations between crystalline and amorphous phases, and a smooth surface of the gas bubbles would be expected.

As discussed previously,² the tensile properties of gas-filled polymers cannot be predicted by a simple model based on two-phase mechanics. Such a model,⁹ considering the polymer to be a continuous matrix and the gas bubbles to act as discrete filler particles, would predict a monotonic reduction in both elongation to break and tensile strength with increasing volume fraction of gas bubbles. The results of the present study, where no distinct differences are evident between samples containing gas bubbles and those free of such bubbles, are in clear disagreement with the predictions of such simple two-phase mechanics.

The effects of gasification on the tensile properties and drawing behavior of the two amorphous polymers are also strikingly different from those observed with PE. In PE, both the yield stress and elongation to fracture are reduced (the latter dramatically) due to a fracture process associated with the gas bubbles. In both PC and PVC, neither property shows appreciable variation between gasified and ungasified material. The presence of the bubbles also appears to have little effect on the drawing behavior of the amorphous polymers. Where they could be observed (Fig. 2), the bubbles change during drawing from their original spherical shape to elliptical shapes oriented with the long dimensions in the drawing direction. No growth or expansion of the bubbles at the expense of neighboring unbubbled regions could be detected.

The marked embrittlement of the semicrystalline polymers upon development of a gas bubble structure reflects a failure of the strain-hardening process required for stable neck formation. Maxima are often observed in load-elongation curves, but these are followed by failure rather than by extensive drawing. The results of the present investigation suggest that

the embrittlement is associated with the structural changes which take place during crystallization, and not merely with access of the gas to the interior regions of the specimens.

Under load, stress intensification is expected at the peripheries of spherical bubbles, with the maximum tensile stresses occurring at the sides of the bubbles, tending to enlarge them in a direction normal to the applied stress. Such enlargement would be expected were the polymers to fail in a brittle manner. The observed elongation parallel to the draw direction indicates that the stress concentration due to the bubbles is insufficient to cause brittle failure. It suggests a strengthening of the material at the sides of the voids, very likely by orientation in the direction of applied stress, so that the higher stress level can be supported and the material behave in a ductile manner.

Both nitrogen and helium gasification lead to similar values of the tensile properties and to similar changes in drawing behavior, despite the presence of observable bubbles in only the nitrogen-gasified material. This indicates again the lack of a significant direct influence of the gas bubbles on the mechanical behavior. The physical basis of the effects of gasification on the phenomenological tensile behavior are not satisfactorily clear—for example, why gasification should prevent the formation of shear bands in PC or why it should change the response of PVC from necking and cold-drawing to uniform drawing.

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References

1. A. G. Kolbeck, D. R. Uhlmann, and P. D. Calvert, *J. Appl. Polym. Sci.*, **17**, 679 (1973).
2. A. G. Kolbeck, D. R. Uhlmann, and P. D. Calvert, *J. Appl. Polym. Sci.*, **17**, 695 (1973).
3. C. J. Benning, *Plastic Foams*, Interscience, New York, 1969.
4. H. Schnell, *Chemistry and Physics of Polycarbonate*, Interscience, New York, 1964.
5. J. B. Park and D. R. Uhlmann, *J. Appl. Phys.*, **49**, 2928 (1970).
6. A. S. Michaels and H. J. Bixler, *J. Polym. Sci.*, **50**, 413 (1961).
7. V. T. Stannett, in *Diffusion in Polymers*, J. Crank and G. S. Park, Eds., Academic Press, New York, 1968, Chap. 2.
8. D. W. Van Krevelen, *Properties of Polymers—Correlations with Chemical Structure*, Elsevier, Amsterdam, 1972.
9. L. E. Nielsen, *J. Appl. Polym. Sci.*, **10**, 97 (1966).

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