

# Primers for Adhesive Bonding to Polyolefins

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## SYNOPSIS

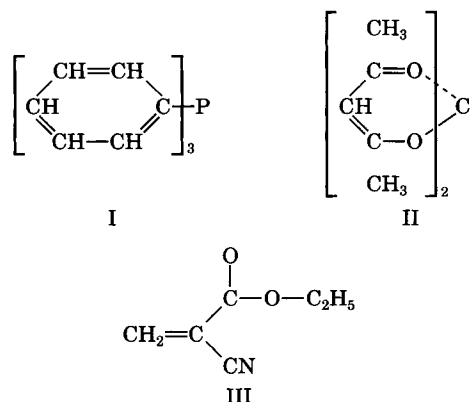
When polypropylene (PP) and low density polyethylene (LDPE) are coated with about 100 nm of triphenylphosphine (TPP) or cobalt acetylacetonate ( $\text{CoAcac}_2$ ) primers, adhesive bonds can be made using ethyl cyanoacrylate (CA) adhesive. These bonds are sufficiently strong so that the bond strength exceeds the bulk shear strength of the polyolefin, and are sufficiently durable as to withstand immersion in boiling water for long periods of time. The dependence of adhesive bond performance on primer thickness, application solvent, aging of primed surface, and the durability of bond, are explained on the basis of a model where the primer dissolves in the polymer surface and facilitates interpenetration of the polyolefin and the monomeric CA. The primer catalyzes cure of the CA, resulting in entanglement of adhesive and adherend chains. This model is tested using infrared (IR) spectroscopic, x-ray spectroscopic (XPS), and microscopic (SEM) analysis. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

The concept of "priming" a surface before making an adhesive bond is widely recognized when dealing with metals, but is less so when dealing with plastic substrates. However, some surface modification is necessary for low surface energy polymers, such as low density polyethylene (LDPE) or polypropylene (PP), if adequate adhesive bonds are to be formed. Currently, the most widely used surface modification techniques for such materials are corona discharge, plasma modification, or treatment with an oxidizing acid,<sup>1,2</sup> often in conjunction with mechanical roughening of the surface. The inconvenience of such treatments, together with questions about the durability of adhesive bonds to such modified surfaces, has stimulated research into alternative surface modification techniques.

It has been reported that polyolefin surfaces can be modified by application of solutions of such diverse materials as chlorinated polyethylene oligomers, transition metal complexes, and organic bases, which improves adhesive bonding with cyanoacrylate adhesives.<sup>3-6</sup> Mechanistic interpretations are

either absent or (as we will show later) implausible. We have described in a series of conference presentations our initial evidence concerning the mechanism of adhesion promotion.<sup>7-9</sup> The purpose of this article is to provide a detailed interpretation of the mechanism by which triphenyl phosphine (TPP, structure I) and cobalt acetylacetonate ( $\text{CoAcac}_2$ , structure II) improve the performance of polyolefin adhesive bonds with ethyl cyanoacrylate adhesive (CA, structure III).



Cyanoacrylate adhesives are particularly useful for repair or rapid fabrication applications, because of their low viscosity and the rapid cure of the adhesive in the presence of a base. The polymerization

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is thought to occur by an anionic mechanism.<sup>10,11</sup> With unmodified polyolefins, the mechanical properties of CA/polyolefin adhesive joints are poor.

## EXPERIMENTAL

The CoAcac<sub>2</sub> and TPP were of reagent grade (Aldrich Chemicals) and were used as received. The CA monomeric adhesive was provided by Loctite Corporation and contained 10 ppm of a proprietary acidic polymerization inhibitor. The primers were applied by spraying a dilute solution (0.03–0.5 wt %, usually in toluene) onto the polymer surface, and allowing the solvent to evaporate in ambient air. Calculation of the amount of primer applied (or the apparent thickness of the primer layer) was performed by a separate calibration of the spraying procedure on LDPE films and then by analysis of the quantity of primer applied by transmission infrared (IR) spectroscopy. The amount of primer applied was controlled by varying the concentration of the primer solution.

Adhesive bonds were of the single lap shear type, constructed using 25 × 25 × 6 mm blocks of PP and LDPE. The polyolefin blocks were cleaned by Soxhlet extraction with acetone before use. Unless stated otherwise, adhesive bonds were made within 30 min of application of the primer. A constant volume of CA adhesive (0.05 cm<sup>3</sup>) was placed on the surface of one block, then the adhesive bond was made with the second block using light finger pressure until the adhesive "set" (< 1 min). At least two days were allowed for completion of the cure before testing. The shear strength of the joints was measured according to ASTM D4501-85. Fracture surfaces were examined by scanning electron microscopy, using an Amray 1200B SEM and gold-coated specimens to reduce charging in the electron beam.

Aging studies were conducted both on the primed polyolefin surfaces (exposure to ambient air or in a forced air oven) and on the adhesive bonds (immersion in boiling water). The aging characteristics of the primed surfaces were followed by the change in water contact angle (NRL 200-00 goniometer), IR-IRS spectroscopy (see below), and changes in adhesive bond strength. The aging characteristics of the adhesive bonds were evaluated as the time of immersion in boiling water required for the adhesive bond to delaminate spontaneously.

The diffusion characteristics of the primers were followed by Fourier Transform Infrared (FT-IR) spectroscopy. The diffusion coefficient of TPP in

polypropylene at 100°C was estimated by placing a drop of molten TPP on the polymer surface, and allowing the primer to penetrate the polymer for 1–15 h. The specimen was then allowed to cool to room temperature and a section of about 25 micrometer in thickness was cut perpendicular to the surface of the block using a microtome. The depth to which the TPP had diffused into the PP was then determined by IR microscopy (Spectratech IR-Plan microscope, interfaced with a Nicolet SX-60 FT-IR, operated at 4 cm<sup>-1</sup> resolution). The diffusion characteristics of TPP and CoAcac<sub>2</sub> in polyolefins under ambient conditions were determined by coating an 100-micrometer thick LDPE film in the conventional fashion, then placing the primed surface in contact with a germanium internal reflection spectroscopy (IRS, 60° incidence) element. The characteristic IR absorptions of either TPP or CoAcac<sub>2</sub> were followed as a function of time. The principle of the method is that as the primer diffuses away from the polymer surface, the intensity of the IR-IRS absorptions will decrease, until that portion of the primer which diffuses further than the sampling depth of the IR-IRS element (about 200–400 nm micrometers for these optical conditions, depending on wavelength) becomes "invisible" to the IR beam.

The effect of the primers on the polymerization kinetics of the CA was followed using a specially constructed IR cell with LDPE windows. Films of LDPE, 100 micrometers thick, were compression-molded from commercial polymer pellets (Aldrich) and were cleaned by Soxhlet extraction with acetone. These films were then used as the windows of a flow-through transmission IR cell with an 100-micrometer Teflon spacer. The monomeric adhesive was injected into the cell using a syringe, and the FT-IR spectrum was collected at 4 cm<sup>-1</sup> resolution every 10 sec. The effect of the primed surface on polymerization kinetics was determined using LDPE windows, which had been coated with primer in the conventional fashion.

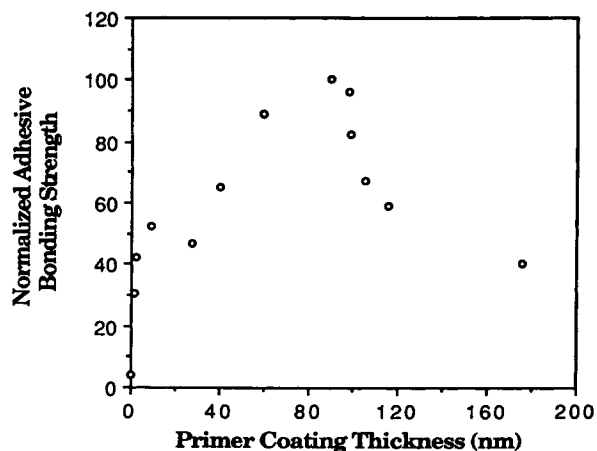
The miscibility of the primers with polyolefins was determined by differential scanning calorimetry (DSC, DuPont 990). Weighed amounts of primer and polymer were placed in a DSC pan and were heated at 10°C/min to 140°C, then were cooled rapidly before repeating the thermal cycle several times. The reduction in the melting endotherm of TPP at about 80°C, and the depression of the melting point of the polyolefin, were used as indications of molecular level mixing of the primer and polymer.

The possibility of molecular interpenetration of the CA adhesive and the primed polyolefin surface was investigated by a series of solvent extractions,

followed by spectroscopic analysis of the extracted polymer surfaces. Adhesive bonds were prepared using one primed and one unprimed polyethylene substrate. This allowed the cyanoacrylate adhesive layer to be exposed by mechanical stripping of the unprimed surface. The exposed adhesive layer was then washed with solvents chosen to be good for CA, but to have varying solvent power for the polyethylene surface. If interpenetration of the CA and the polyethylene had occurred, then some CA would remain trapped in the polyethylene surface if the chosen solvent was unable to swell the polyethylene. Therefore, after washing with the solvent for CA, the remaining polyethylene surface was examined by IR-IRS and x-ray photoelectron spectroscopy (XPS, PHI 10-400, monochromatized Al  $K_{\alpha}$  radiation). The optical conditions for the IR-IRS experiment and the take-off angle for the XPS experiment were varied so as to obtain a concentration depth profile of CA functionality in the polyethylene surface.

## RESULTS

Figure 1 shows the dependence of adhesive bond strength on the apparent thickness of the CoAcac<sub>2</sub> primer layer on PP. The term "apparent" is used because, as we will show later, the primer dissolves in the polyolefin surface. However, even though the thickness term has no physical meaning, it remains a useful parameter to assist in visualizing the extent of modification of the surface. Clearly, the optimum modification of the polyolefin surface is at levels of



**Figure 1** The dependence of joint strength on apparent primer thickness for adhesive joints constructed from CA and CoAcac<sub>2</sub>-primed PP.

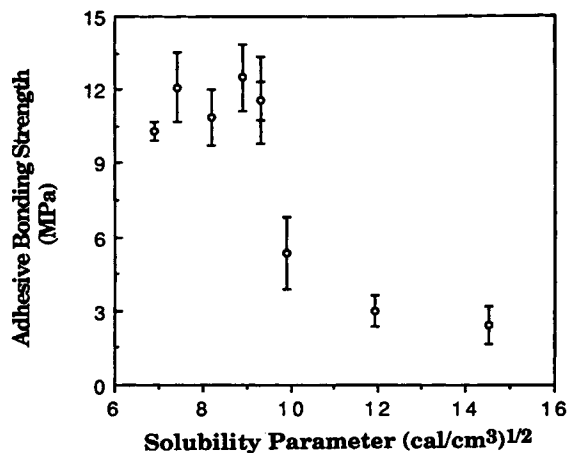
**Table I** Durability of Adhesive Bonds in Boiling Water

Substrate	Surface Treatment	Adhesive	Lifetime (h)
PP	None	CA	< 1
PP	Plasma	CA	20
PP	TPP Primer	CA	90

primer orders of magnitude greater than monomolecular coverage. Similar relationships were also found for the TPP primer and for LDPE substrates, although the exact position of the optimum depends on the solvent used for application of the primer and the extent of aging of the primed surface before application of the adhesive (see below). The maximum joint strength obtained corresponded in all cases approximately to the shear strength of the bulk polyolefin, that is, the limiting case for good adhesion.

Table I shows that adhesive bonds formed with the TPP primer were durable as well as strong. Without primer, the PP/CA adhesive bonds had little strength and delaminated almost immediately on contact with boiling water. A "conventional" surface preparation procedure (5 min in an *rf*-induced air plasma) increased both the initial strength and durability, but, when the TPP primer was used, a further appreciable increase in durability was achieved. This could be due to the interpenetration of the CA and polyolefin, as will be demonstrated below. No attempt was made to further refine the primer formulation or application procedure to optimize the property of durability.

The nature of the application solvent had a significant effect on the strength of the resultant adhesive bond (Fig. 2). The TPP primer was applied at a constant apparent thickness, but from solvents with different solubility parameters. Optimum adhesion was achieved when a solvent was chosen that could swell the polyolefin surface, that is, it had a solubility parameter close to that of polyolefins (about 8–9 (cal/cm<sup>3</sup>)<sup>1/2</sup>). A complete analysis of this effect should also include the effect of apparent thickness for each solvent, but the data in Figure 2 should be adequate to illustrate the principles involved. Note that the choice of solvents was limited to those which would dissolve the primer and did not react with the primer; solvents were also chosen to have critical surface tensions that were lower than that of the polymer, so as to allow wetting of the surface.

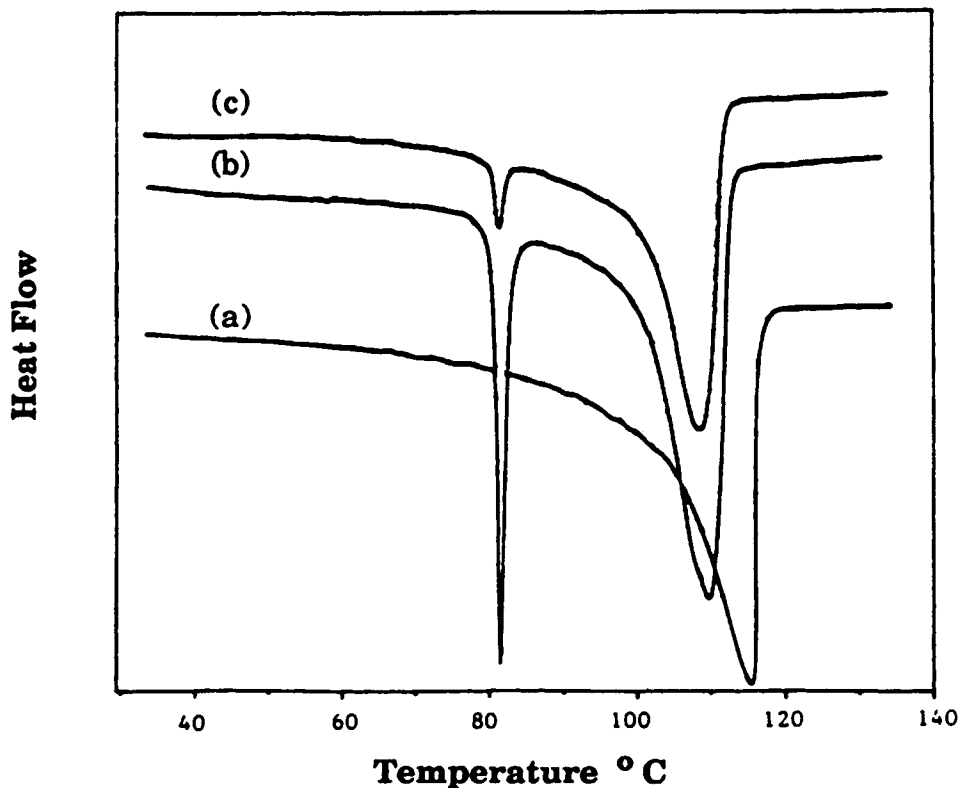


**Figure 2** The dependence of joint strength on the solubility parameter of the application solvent for adhesive joints constructed from CA and TPP-primed PP. Apparent primer thickness constant at approximately 100 nm.

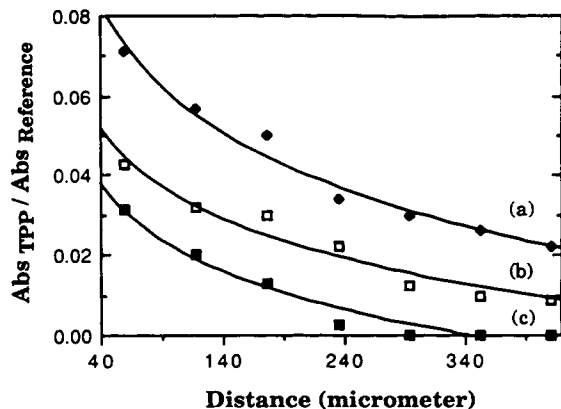
The data in Figures 1 and 2 imply that the miscibility of the primer in the polyolefin is important to its function. Figure 3 demonstrates that TPP primer is miscible with LDPE even at high primer

concentrations (50% by weight of TPP). On the first thermal cycle, the crystalline TPP powder had not had the opportunity to mix with the LDPE, and so a sharp TPP melting endotherm was observed at about 80°C [Fig. 3(b)]. During continued heating of the sample, the molten TPP dissolved in the LDPE and so decreased the polymer melting point [compare Fig. 3(b) with Fig. 3(a)]. On a subsequent heating cycle, the majority of the TPP has dissolved in the LDPE and so no longer exhibited a separate crystalline melting point [Fig. 3(c)]. Therefore, it is concluded that TPP is miscible with LDPE. Similar behavior was observed for TPP in PP. With CoAcac<sub>2</sub>, the melting point was above its decomposition temperature and so the DSC method was not useful. However, after heating a mixture of CoAcac<sub>2</sub> and LDPE to 150°C, what appeared visually to be a homogeneous mixture was produced, with a uniform pink color, implying that miscibility with the polyolefin surface was a common feature for the primers.

Given that mixing of the primer and the polyolefin is the preferred equilibrium state (Fig. 3), the kinetics of the mixing process must be considered.



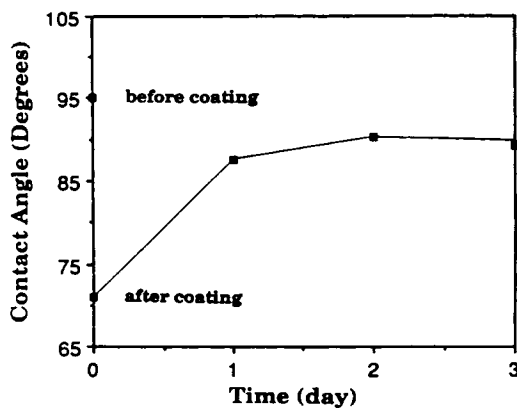
**Figure 3** Melting endotherms of LDPE and 50 : 50 LDPE/TPP mixtures, at 10°C/min heating rate. (a) LDPE, (b) LDPE/TPP, first heating cycle, and (c) LDPE/TPP, second heating cycle.



**Figure 4** Concentration profile of TPP in PP surface after various times of contact of molten TPP with PP surface at 100°C. (a) 15 h, (b) 5 h, and (c) 1 h. Relative concentration calculated as ratio of integrated absorbances centered at 1090  $\text{cm}^{-1}$  (TPP) and 2714  $\text{cm}^{-1}$  (PP).

Figure 4 shows the concentration profiles of TPP in PP, which occurred after various times at 100°C. The data were obtained by IR microscopy of thin sections cut perpendicular to the PP surface. Clearly, diffusion was possible on a dimension scale of hundreds of micrometers and, if the boundary condition is assumed to be pure TPP (a reasonable assumption for a drop of molten PP sitting on the PP surface), then a diffusion coefficient of  $8 \times 10^{-13} \text{ cm}^2/\text{s}$  can be calculated.

While informative as to the general mobility of a primer in a polyolefin, the data in Figure 4 tell little about how far the primer will penetrate during the conventional application procedure (when a solvent is also present), or the aging characteristics of a primed surface under ambient conditions. It is apparent from the changes in water contact angle



**Figure 5** Advancing contact angle of water at 25°C on LDPE as a function of time after application of TPP primer.

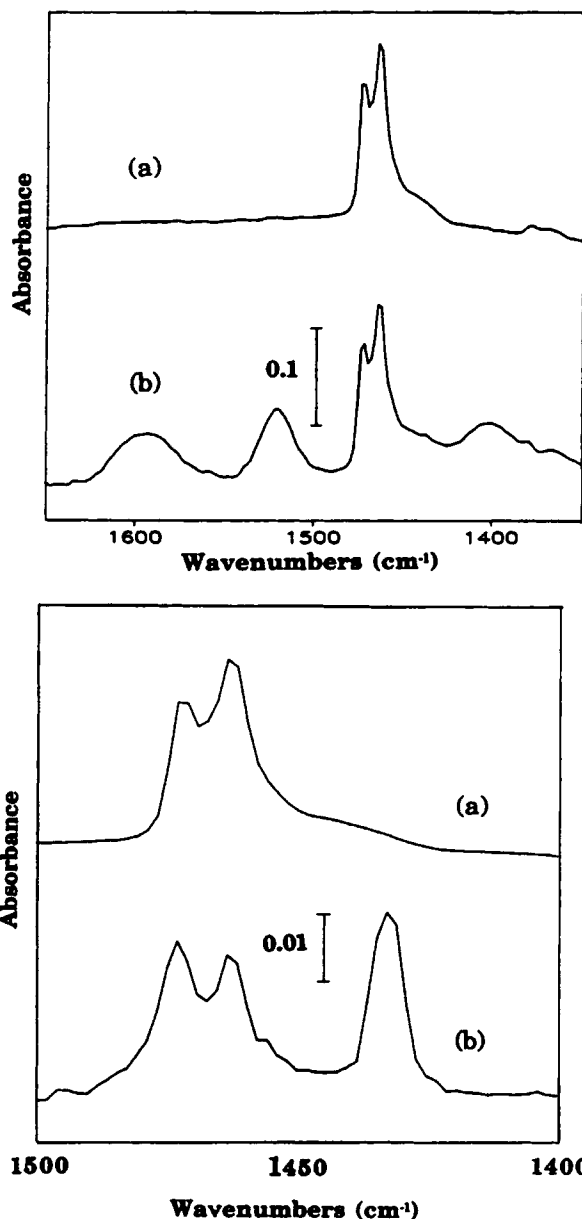
**Table II** Aging of Primed Polymer Surfaces

Surface	Shear Strength (MPa)
TPP-Primed PP, Unaged	12.5
TPP-Primed PP, 24 h at 25°C	1.4
CoAcac <sub>2</sub> -Primed PP, Unaged	12.7
CoAcac <sub>2</sub> -Primed PP, 24 h at 25°C	9.3
CoAcac <sub>2</sub> -Primed PP, 12 h at 80°C	2.7

(Fig. 5) that the characteristics of the surface change with time. The 25° drop in contact angle, which occurs after priming of LDPE with TPP, was reversed on aging until after 2–3 days, when the surface had almost returned to its original low energy state. This increase in contact angle coincides with a decrease in bondability of the primed surface (Table II). It is noteworthy that the CoAcac<sub>2</sub>-primed surface ages more slowly than the TPP-primed surface, but that after a sufficiently long time, both primed surfaces return to their original low bondability state. Water contact data were not available for the CoAcac<sub>2</sub> primed surface because of the significant solubility of CoAcac<sub>2</sub> in water.

Because it was anticipated that primer migration during application or during ambient aging would be on a dimension scale appreciably smaller than the high temperature aging data in Figure 4, the IR-IRS technique was chosen to follow the ambient diffusion process. Figure 6.1 shows the IR-IRS spectrum of a CoAcac<sub>2</sub>-primed LDPE surface. Characteristic absorptions of the primer are readily quantifiable (1589, 1517, 1400  $\text{cm}^{-1}$ ), and so the apparent concentration of primer in the surface could be followed as a function of time. As the primer diffuses into the bulk of the polymer, it moves further from the IRS element surface, and so is sampled less sensitively by the IR beam. Under these optical conditions (wavelength, refractive indices, and angle of incidence), the intensity of the evanescent wave from the element has diminished by 70% at about 300 nm from the surface; thus the extent of coupling of the oscillating molecular dipole to the IR radiation has decreased to less than 10% of its value at the element surface. Figure 6.2 shows the IR-IRS spectrum of a TPP-primed LDPE surface, and illustrates that the absorption at 1435  $\text{cm}^{-1}$  can be used to follow changes in the surface composition.

Figure 7 shows the decrease in characteristic absorptions of both TPP (1435  $\text{cm}^{-1}$ ) and CoAcac<sub>2</sub> (1589  $\text{cm}^{-1}$ ) primers in the surface of LDPE. Over a period of several days under ambient conditions, appreciable migration of the primer away from the

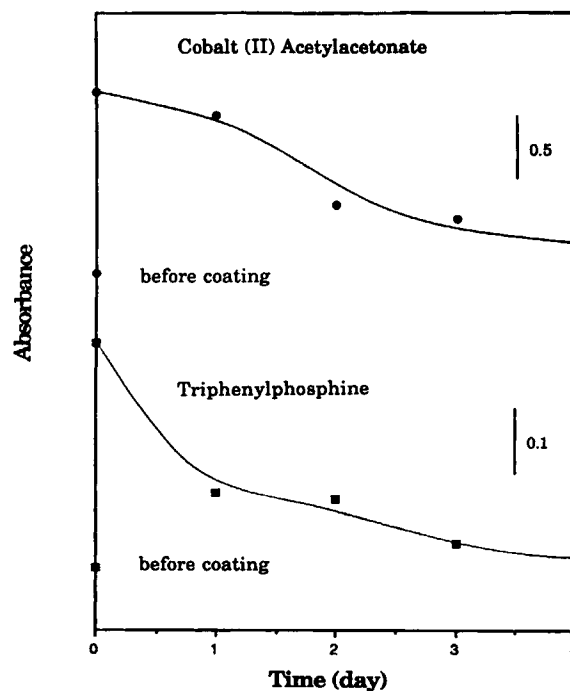


**Figure 6** IR-IRS spectra of [6.1 (a)] LDPE, [6.1 (b)] CoAcac<sub>2</sub>-primed LDPE, [6.2 (a)] LDPE, and [6.2 (b)] TPP-primed LDPE.

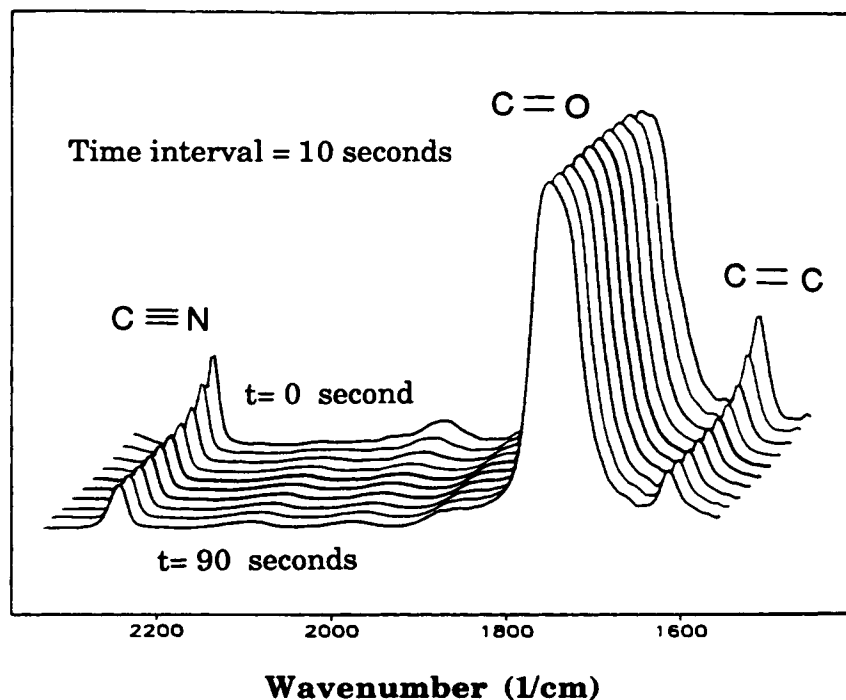
surface is observed. It is also gratifying to note that the relative migration of the primers (TPP > CoAcac<sub>2</sub>) matches the relative rate at which the primed surface loses its bondability (Table II) and, in the case of TPP, matches the change in contact angle (Fig. 5). In order to confirm that diffusion of the primer away from the surface was the principal cause of loss of bondability, several other qualitative experiments were performed to eliminate other possible causes. Volatilization of the primer was a pos-

sibility, but this possibility was eliminated as a cause for the aging phenomenon by monitoring the mass loss from a thin film of primer both by gravimetry and by transmission IR spectroscopy; insignificant mass loss was observed under ambient conditions. Reaction with oxygen or carbon dioxide was another possible cause of aging, but this possibility was eliminated by aging specimens in pure nitrogen and pure carbon dioxide; no differences from aging in air were detected. Also, if the TPP was intentionally oxidized (partial conversion to triphenyl phosphine oxide by heating in air at 100°C for 18 h) before application to the surface, no difference in primer effectiveness was detected. In fact, pure triphenylphosphine oxide (Aldrich) functioned as a moderately effective primer.

The presence of primer had an appreciable effect on the kinetics of CA polymerization. Figure 8 shows the changes in the IR spectrum as CA polymerized. The characteristic absorptions of the nitrile, carbonyl, and vinyl functionality all changed during the polymerization. This was because of the delocalized nature of the bonding in the cyanoacrylate functionality. The absorbance characteristic of carbonyl functionality (it is realized that IR absorptions are not localized to one pair of atoms, but in this



**Figure 7** Integrated absorbance of characteristic absorptions of CoAcac<sub>2</sub> (1589 cm<sup>-1</sup>) and TPP (1435 cm<sup>-1</sup>) primers in the IR-IRS spectra of LDPE surfaces, as function of time of aging of the surface at 25°C.



**Figure 8** A representation of the changes that occur in the IR spectrum of CA as it polymerizes. Transmission IR spectra were obtained using a cell with TPP-primed LDPE windows.

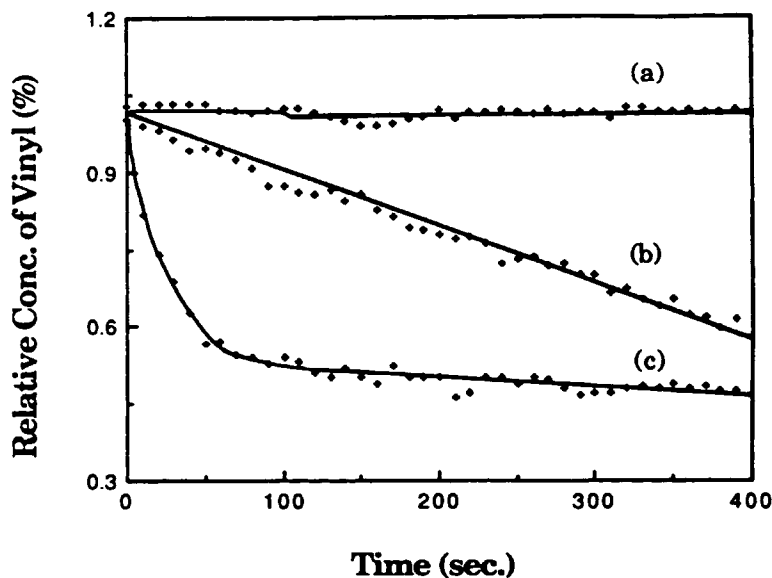
case, vibrational coupling to other atoms is slight) remained approximately constant in intensity, but increased in frequency by about  $10\text{ cm}^{-1}$  when removal of the conjugation to the vinyl group raised the force constant for the  $\text{C}=\text{O}$  bond. The absorption of the nitrile group ( $2237\text{ cm}^{-1}$ ) changed in both intensity and frequency, again because of a change in the extent of resonance when polymerization occurred. The vinyl absorption at  $1611\text{ cm}^{-1}$  would be eliminated if the polymerization was complete, and so the integrated absorbance of this band was used to monitor the polymerization rate.

Figure 9 shows that in the absence of primer, the rate of polymerization was slow. Both  $\text{CoAcac}_2$  and TPP-primed LDPE windows to the IR cell caused a marked increase in the polymerization rate. It is also significant that, following an initially rapid reaction, the cure did not progress above about 60% completion. This is attributed to the effect of vitrification of the polymerizing CA. Almost complete consumption of the vinyl functionality occurred only after several days, or on raising the temperature to above  $80^\circ\text{C}$  for several hours.

When priming was performed at close to the optimum conditions (see above), failure during the shear testing of the adhesive joints occurred cohe-

sively within the polyolefin substrate. Figure 10 shows the fracture surface of the PP substrate after failure of a TPP-primed PP/CA/PP adhesive bond. The extensive plastic deformation and fibrillation is characteristic of a ductile failure within the PP. Cohesive failure within the CA would yield a much smoother fracture surface, since the polymerized CA is a brittle material. The assumption that cohesive failure occurred within the polyolefin was also supported by the value for the adhesive bond strength (Fig. 1), which was close to the shear strength of bulk PP, and by dye uptake experiments (the CA readily accepted a dye while PP did not; the failure surface showed no dye uptake by optical microscopy).

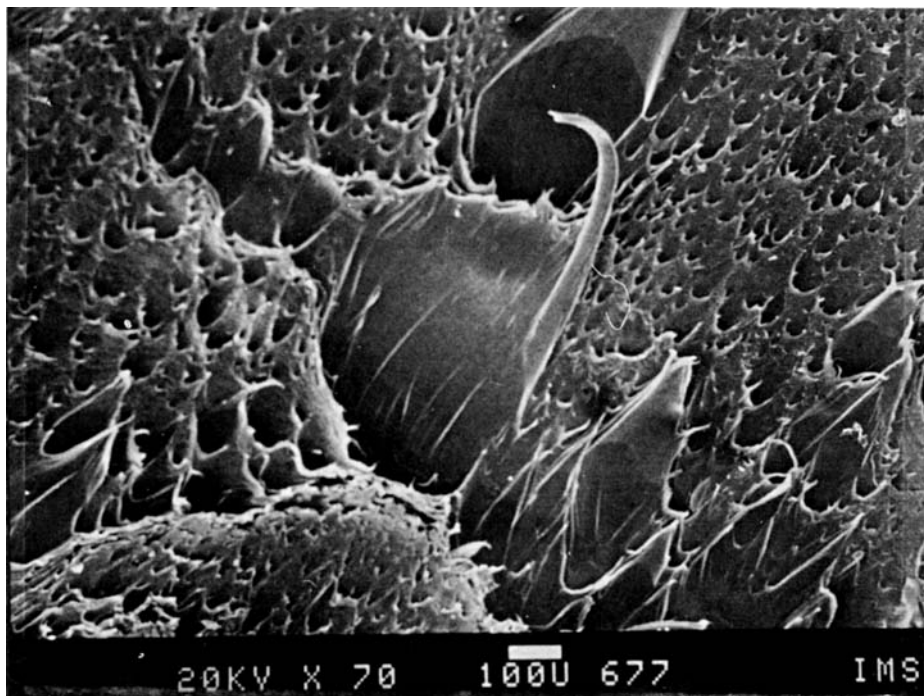
In order to test the hypothesis that some interpenetration of adhesive and adherend had occurred, solvent extraction experiments were performed on CA/LDPE interfaces, as described in Experimental. When unprimed LDPE was used as the substrate, the polymerized CA could be washed off completely by any good solvent for CA. The IR-IRS spectrum of the surface of the washed substrate was then identical to that of the original LDPE (data not shown). When a TPP-primed substrate was used, a significant amount of the polymerized CA could



**Figure 9** The change in integrated intensity of the vinyl absorption at  $1611\text{ cm}^{-1}$  by transmission IR, using cell with LDPE windows (a) unprimed, (b) CoAcac<sub>2</sub>-primed, and (c) TPP-primed.

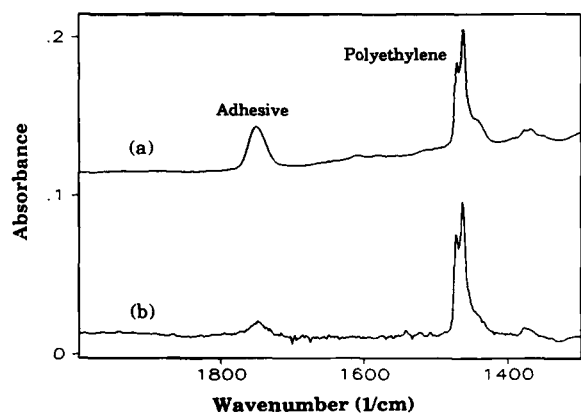
not be removed from the surface by washing with nitromethane (a good solvent for CA, but a poor solvent for LDPE). The IR-IRS spectrum of such a washed surface is shown in Figure 11(a), which

exhibits the characteristic carbonyl stretch absorption of polymerized CA at  $1750\text{ cm}^{-1}$ . This could be ratioed in intensity to the C—H bending mode of polyethylene at  $1463\text{ cm}^{-1}$  to obtain a measure of



**Figure 10** SEM of the PP substrate after fracture of an adhesive joint constructed from CA and TPP-primed PP.





**Figure 11** IR-IRS spectra of LDPE surfaces after attempted removal of CA adhesive by washing with (a) nitromethane and (b) acetone. TPP-primed LDPE examined using KRS-5 IRS element and 45° incidence.

concentration of the CA in the LDPE surface. A calculation of concentration data was made by comparison of the absorbance ratios of the IR-IRS spectra to the ratio of extinction coefficients of corresponding functional groups, after correcting the IR-IRS spectra for the wavelength of the sampling depth.<sup>12</sup>

With a KRS-5 element and 45° incidence, the sampling depth of IR-IRS in this region was about 1000 nm, and so the concentration information referred to an average over this sampling depth. Separate IR-IRS measurements were also made with a germanium element at 45° incidence (sampling depth 500–600 nm) and at 60° incidence (sampling depth approximately 200–300 nm). The relative concentration data are presented in Table III. In order to obtain information about CA concentration at shallower depths, we examined the same surfaces by XPS spectroscopy. The sampling depth was about

10 nm under these conditions, and the relative concentration of CA and LDPE in this thin surface layer could be calculated from the ratio of the C1s and N1s signals [Fig. 12 (a)], after correction by appropriate atomic sensitivity factors. It was confirmed that the N1s signal originated from the CA, not from residual nitromethane, from its characteristic electron energy (400 eV), which was typical of nitrile nitrogen rather than oxygenated nitrogen. The data in Table III show that a concentration profile of CA in LDPE occurs at about 1 micrometer, although the majority of the CA is within the first few tens of nanometers.

When the CA adhesive layer was washed with a better solvent for the LDPE, and still a good solvent for CA, some swelling of the substrate surface occurred, and most of the CA could then be extracted. This can be seen by the reduction in carbonyl intensity by IR-IRS [Fig. 11 (b)] and the elimination of the N1s signal by XPS [Fig. 12 (b)], when acetone (solubility parameter close to that of LDPE) was used as the washing solvent. A solvent of intermediate ability to swell the LDPE surface (acetonitrile) left an intermediate amount of CA (Table III). This demonstrated that a mixing phenomenon, rather than covalent bonding, was responsible for interpenetration of polymerized CA and the polyolefin.

## DISCUSSION

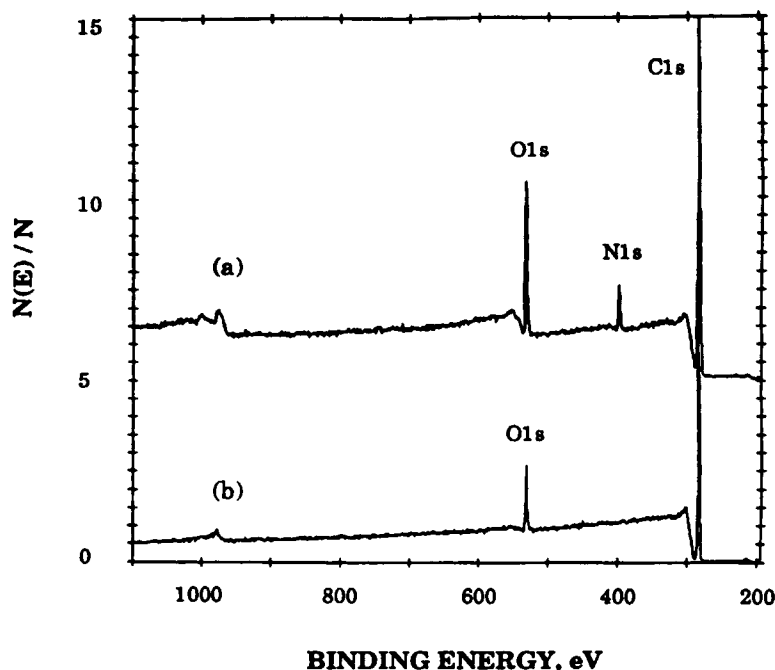
The promotion of polyolefin–cyanoacrylate adhesion by the use of TPP and CoAcac<sub>2</sub> primers has aspects of chemistry, physics, and fracture mechanics. The above data can be reconciled by first considering the structure of the primed surface, then the structure of the adhesive bond, and finally some qualitative

**Table III** Concentration Profile of Penetrating CA Adhesive<sup>a</sup>

Solvent	Solub. Param.	Analysis Method	Sampling Depth	Conc. of CA <sup>b</sup>
Nitromethane	12.9	IR-IRS, KRS-5, 45°	ca. 1000 nm	0.7
Nitromethane	12.9	IR-IRS, Germanium, 45°	500–600 nm	1.2
Nitromethane	12.9	IR-IRS, Germanium, 60°	200–300 nm	1.6
Nitromethane	12.9	XPS, 62° Take-off	ca. 10 nm	7.1
Acetonitrile	11.7	XPS, 62° Take off	ca. 10 nm	3.9
Acetone	8.9	XPS, 62° Take off	ca. 10 nm	0

<sup>a</sup> TPP-primed LDPE after washing with good solvent for CA.

<sup>b</sup> Number of CA repeat units/100 CH<sub>2</sub> units of LDPE.

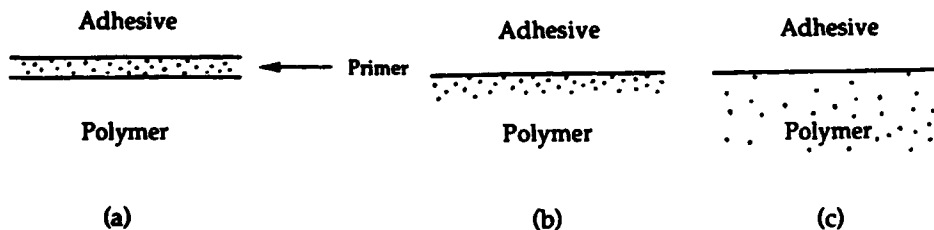


**Figure 12** XPS spectra of LDPE surfaces after attempted removal of CA adhesive by washing with (a) nitromethane and (b) acetone. TPP-primed LDPE was examined at a  $62^\circ$  take-off angle.

observations on other polymers to support the proposed model.

The polymer surface after application of the primer was not in an equilibrium state. Figures 3 and 4 indicate that, after infinite time, the primers should become dispersed in the bulk of the polymer, and considerations of surface energetics (Fig. 5) indicate that the primer should be excluded from the surface. It was, therefore, not surprising that the primers diminish in effectiveness with aging time before application of the adhesive (Table II). These data may be rationalized in cartoon terms as shown in Figure 13. If the primer is immiscible with the polyolefin, it will remain deposited as a thin film on

the polymer surface, and thus will fracture as a weak boundary layer. At the other extreme, a miscible primer after prolonged aging will diffuse away from the polymer surface, and so cannot influence the adhesion to polycyanoacrylate. The optimal condition is for the primer to penetrate the polymer surface, producing a surface layer with mechanical integrity, but with modified surface energetics and chemical functionality. The role of the application solvent (Fig. 2) is then to swell the polymer surface and so facilitate penetration of the primer. The apparent effect of primer thickness (Fig. 1) is in fact a dynamic effect. If the amount of primer applied is too small, it may be insufficient to facilitate inter-

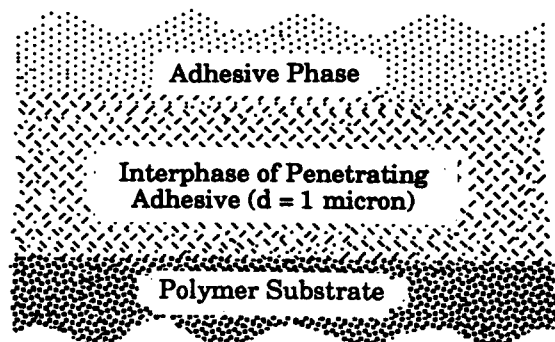


**Figure 13** A schematic representation of the state of the primed surface (a) insoluble primer forming weak boundary layer, (b) primer dissolved in the polymer surface, and (c) primer dissolved in the bulk of the polymer.

penetration (see below), but also it may have diffused away from the surface before formation of the adhesive bond. If the amount of primer applied is too large, then the surface loses its mechanical integrity, and so the adhesive bond strength is reduced.

Assuming that the optimal polyolefin surface characteristics have been obtained, we can then consider what happened when the cyanoacrylate adhesive was applied. The first criterion for adhesive bonding is that the adhesive must wet the adherend. We have not attempted to determine the magnitude of the critical surface tension<sup>13</sup> of the primed surface through contact angle measurements with various liquids, because of the solubility of the primers in most organic solvents. However, in a semiquantitative sense, the benefits of priming to wettability (Fig. 5) are obvious.

There appeared to be no covalent bond formation between adhesive and adherend, as was important for silane coupling agents.<sup>14</sup> A model involving a monolayer of primer on the polymer surface, adhering by a specific chemical interaction with the adhesive,<sup>3</sup> was also inconsistent with our data concerning apparent primer thickness (Fig. 1). Instead, a durable (Table I) adhesive bond was produced by interpenetration of the adhesive and adherend. This is represented in Figure 14. The adhesive bond was sufficiently strong that failure occurred cohesively in the polyolefin substrate (Fig. 10). The resistance of a fraction of the adhesive to extraction with a solvent implied interpenetration with the polyolefin at a molecular level. The cumulative data for adhesive concentration as a function of sampling depth (Table III) indicated that interpenetration had occurred on a dimension scale of up to one micrometer. The extent of interpenetration will depend on at least three factors:



**Figure 14** A schematic representation of molecular interpenetration at the CA/polyolefin interface, with approximate dimension of interpenetrating layer ( $d$ ).

1. The solubility of the monomeric adhesive in the adherend,
2. The rate of diffusion of the monomeric adhesive into the adherend,
3. The rate of polymerization of the adhesive.

The CA/primed-polyolefin system provided an excellent opportunity for such processes to occur. The monomeric adhesive had a low viscosity and had a significant solubility in polyolefins. When the monomer contacts an initiating species, such as a base, polymerization was rapid, and so there was the possibility of chain formation in an entangled state within the polyolefin surface, as supported by data in Figures 11 and 12. This bears some relation to the concept of interpenetrating polymer networks described by Sperling,<sup>15</sup> but described here is a thin region of continuously changing composition rather than a unique material.

This model was supported by several other qualitative observations on the effectiveness of primers for other adhesives and substrates. These primers were effective in promoting adhesion of CA to silicone rubber, but not to fully fluorinated polymers (e.g., Teflon). This implied that low surface energy was not the requirement for a substrate, rather a material which the primer can penetrate. Primers have some effectiveness in epoxy/polyolefin adhesive bonds, although the manner of application has to be modified from that described here. The implication here is that a viscous adhesive may not penetrate sufficiently before polymerizing. A wide range of materials appear to be capable of functioning to some degree as primers,<sup>3-6</sup> which does not support the involvement of specific chemical interactions. The principle of an easily applied additive, which facilitates interpenetration of adhesive and adherend, has many other potential applications in adhesive science, and to polymers in general. We continue to explore some of this potential.

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## REFERENCES

1. H. Schonhorn, F. W. Ryan, and R. H. Hansen, *J. Adhesion*, **2**, 92 (1970).

2. R. C. Snodgren, *Handbook of Surface Preparation*, Palmerston, New York, 1972.
3. K. Kimura and Y. Ito, *Kogyo Zairyo*, **34**(3), 74 (1986).
4. K. Ito, European Patent Application, 0129069.
5. Y. Okamoto and P. Klemarczyk, U. S. Patent, 4,979,993, Dec. 1990.
6. C. Nakado and K. Nagazawa, *Japan Patent Office Patent Disclosure Bulletin*, 61-136567, June 24, 1988.
7. A. Garton and J. Yang, *Proc. Amer. Chem. Soc.*, PMSE Div., **62**, 916 (1990).
8. J. Yang and A. Garton, *Proc. Amer. Chem. Soc.*, PMSE Div., **65**, 255 (1991).
9. J. Yang and A. Garton, Proc. 15th Ann. Meeting, Adhesion Society, Hilton Head, SC, Feb. 1992, pp. 43-45.
10. J. P. Cronin and D. C. Pepper, *Makromol. Chem.*, **189**, 85 (1988).
11. S. A. Hurley and P. J. T. Tait, *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 1565 (1976).
12. A. Garton, *Infrared Spectroscopy of Multicomponent Polymer Materials*, Hanser, New York, to appear.
13. W. A. Zisman, *Adv. Chem. Ser.*, **43**, 1 (1964).
14. C. H. Chiang, H. Ishida, and J. L. Koenig, *J. Colloid. Interface. Sci.*, **74**, 396 (1980).
15. L. H. Sperling, *Interpenetrating Polymer Networks and Related Materials*, Plenum, New York, 1981.

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