(16) Marvel, C. S.; Weil, E. D. *J. Am. Chem. Soc.* **1954**, *76*, 61.
(17) Rubingh, D. N.; Yu, H. *Macromolecules* **1976**, *9*, 681.
(18) Mashimo, S.; Matsuo, K.; Cole, R. H.; Winsor, P., IV; Stockmayer, W. H., in preparation.
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Comment on the Paper of Fahrenholtz and Kwei Concerning the Compatibility of Polymer Mixtures Containing Novolac Resins

In a recent paper published in this journal,[1] Fahrenholtz and Kwei report the results obtained from thermal and infrared spectroscopic studies of a number of polymer blends containing novolac resins. Whereas we believe the results are interesting and pertinent to the overall subject of compatible polymer blend systems, there are nonetheless several factors, primarily concerning the interpretation of the infrared spectra, that deserve comment.

The authors show in Figure 4[1] the infrared spectra of pure polycarbonate (PC), the novolac resin, and a 5% mixture of PC in novolac. In the text the authors state that "the entire carbonyl peak is shifted 20 cm^{-1}, with no portion remaining at the higher value" but upon examination of Figure 4, it is evident this is an overstatement. The band is asymmetric and there is still an obvious contribution at 1770 cm^{-1}. Additionally, Fahrenholtz and Kewi state at a later stage in their paper that "the reason the entire carbonyl peak is shifted in the polycarbonate but not in other cases is that the stringent geometric requirement for hydrogen bonding is more easily met in the relatively unhindered carbonate functional group". While this is a reasonable suggestion it is purely speculative and there is a more obvious reason for the observed frequency shift and the overall shape of the band. PC is a polymer capable of crystallization under favorable conditions where the T_g is depressed by the presence of a plasticizer. We have recently published the results of an FT IR study of the polymer blend system PC–poly(ϵ-caprolactone) (PCL)[2,3] which shows the effect of polymer-induced (PCL) crystallization of PC. The carbonyl stretching frequencies associated with PC in amorphous and preferred ("crystalline") conformations are well separated and occur at 1775 and 1768 cm^{-1}, respectively.[2,3] It is impossible to judge the frequency precision of the spectra shown in Figure 4 of Fahrenholtz and Kwei's paper as they are hand drawn and were obtained on a dispersive instrument but the general shape of the bands is almost identical with those we have observed in the PC–PCL blends. Furthermore, the experimental conditions of sample preparation described by the authors would lead to amorphous PC in the pure state and a semicrystalline PC component in that of the blend.[3] Accordingly, we believe the unique result observed by Fahrenholtz and Kwei for the 5% PC–novolac blend may be explained on the basis of plasticizer-induced crystallization of PC by the relatively low molecular weight novolac resin.

We also believe that the description of the spectra of poly(ethyl methacrylate) (PEMA) and the blend containing 98% novovlac resin, shown in Figure 3 of Fahrenholtz and Kwei's paper, has been overstated. If one were to curve resolve the spectra of the blend, the overall contribution from the lower frequency band would appear quite modest. This suggests that the majority of the carbonyl groups associated with PEMA are not associated with the novolac resin. Fahrenholtz and Kwei suggest that this is due to conformational reasons but this was not substantiated. We are perplexed that in a compatible blend containing a large excess (98%) of the novolac resin only a modest concentration of the carbonyl groups of the PEMA is accessible.

References and Notes

(1) Fahrenholtz, S. R.; Kwei, T. K. *Macromolecules* **1981**, *14*, 1076.
(2) Coleman, M. M.; Varnell, D. F.; Runt, J. P. Paper presented at the Xth Biannual U.S./Japan Polymer Symposium, Palm Springs, CA, Nov 1980 (to be published in *Contemp. Top. Polym. Sci.*).
(3) Varnell, D. F.; Runt, J. P.; Coleman, M. M. *Macromolecules* **1981**, *14*, 1350.

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Reply to Comment on the Paper of Fahrenholtz and Kwei

In our previous paper[1] published in this journal, we reported the results of infrared studies of mixtures of novolac resins with several carbonyl-containing polymers. We observed a 20-cm^{-1} shift in the carbonyl stretching frequency of the blends' spectra relative to the carbonyl frequency in the pure compound. This result was attributed to hydrogen bonding between the carbonyl group and the phenolic OH of the novolac. Coleman and Varnell[2] have questioned the validity of this interpretation on two grounds: (i) the precision of the reported spectra and (ii) the possibility that a more obvious explanation involving crystallinity effects may exist, specifically in the case of the polycarbonate–novolac mixture.

Our original spectra were obtained with a dispersive instrument which admittedly could have contributed to a degree of error in the absolute value of the peak positions and shifts. Subsequent to our publication, Coleman and Varnell[2] found that plasticization of polycarbonate in blends with poly(ϵ-caprolactam) induces crystallinity in the polycarbonate, which results in a lowering of the carbonyl stretching frequency by 7 cm^{-1}. This raises the question of as to whether our reported shifts are indeed substantially larger than 7 cm^{-1}, considering the possible errors in our previous measurements; i.e., Coleman and Varnell suggest that our shifts may be due to crystallinity effects and not hydrogen bonding.

To confirm the validity of our data, we have reexamined several samples using a Digilab Model 15B FT IR spectrometer operating at 2-cm^{-1} resolution (conditions similar to those used by Coleman and Varnell). The carbonyl region of the spectrum of a 2:98 polycarbonate–novolac blend (the novolac is the same as that used in Figure 4, ref 1) is shown in Figure 1. Also shown in Figure 1 is the spectrum of pure polycarbonate showing the carbonyl peak at 1774 cm^{-1}. The absorption band of the blend is asymmetric and obviously includes a contribution from ab-

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