Stability of Continuous Emulsion Polymer Reactors

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Synopsis

The stability of continuous emulsion polymer reactors having steady feed streams was studied. Analysis of a population balance model supported the notion of micelle deprivation as the chief cause of reactor instabilities. Analysis of the moments of the distribution indicated that the system may be uniquely stable in one case. Only one steady-state operating point was predicted for the case where the decrease in the termination rate constant due to the gel effect was neglected.

INTRODUCTION

The mechanistic description of emulsion polymerization was first presented by Harkins.[1] Shortly thereafter Smith and Ewart[2] introduced a mathematical representation of the emulsion polymerization process based on Harkin's original concepts. They solved their recursion relation for three limiting cases. The most widely discussed solution is their case II kinetics, where free radical desorption does not occur and the free radical termination process is very rapid relative to the radical adsorption mechanism. The consequences of these conditions are that the average number of radicals per particle is ½, or that at any time half of the particles contain a single growing polymer chain, while the other half contain none. The understanding of the process has been advanced far beyond these early theories. The reader is referred to the review article by Ugelstad and Hansen[3] and the treatise by Blackley[4] for thorough discussions of the kinetics of emulsion polymerization.

Gershberg and Longfield[5] presented one of the first analyses of continuous emulsion polymerization. Their model, based on Smith–Ewart case II kinetics, agreed fairly well with data collected in their laboratories. There were, however, several unresolved issues from their study.

Sato and Taniyama[6] modeled the emulsion polymer process as though it was a series of bimolecular collisions occurring between the species in the system (free radicals, polymer particles, etc.). Their model did not incorporate variations in properties due to particle size. Sato and Taniyama[7] later showed how their model could be used to analyze the performance of a continuous emulsion polymer reactor. Thompson and Stevens[8] extended their concept to include the free radical desorption mechanism. The advantages, and limitations, of this simplistic bimolecular collision concept were discussed by Thompson and Stevens,[8] and are not repeated here.

The first generation of population balance models for continuous emulsion polymer reactors were those reported by DeGraff and Poehlein[9] and Stevens and Funderburk.[10] Their models involved a particle balance over the whole reactor

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Journal of Applied Polymer Science, Vol. 24, 1925–1934 (1979)

0021-8995/79/0024-1925$01.00

EXPERIMENTAL

Materials

Six polymers were used in this work. Four of these have a comonomer weight ratio of S/BA/MAA = 80/15/5; the others have the comonomer ratios shown in Table I but an apparent molecular weight similar to sample 3, based on nearly equal values of the reduced viscosity. The 80/15/5 materials have already been studied extensively,[7] and their characteristics are given in Table I. As noted elsewhere,[7] the molecular weight parameters, calculated from gel-permeation elution spectra, are intended for comparison purposes and are not reported as absolute values. Glass transition temperatures of the polymers were measured by differential scanning calorimetry using the Perkin-Elmer DSC-2 and linear temperature variations of 2.5°C/min. All materials were synthesized and donated by the Paint Research Laboratory, Canadian Industries Ltd, Toronto; they were supplied as dry, free-flowing powders and were used without further purification.

Procedures

The design and operation of the tgb has been discussed previously.[1,2] In the present work the instrument was operated isothermally at 30.0 ± 0.5°C in a laboratory space maintained at that temperature. In one experimental series, a linear thermal gradient was established on the metal bar, with the cold end at 30°C and the hot end at 82°C. Details of operation were those described in the earlier papers. Polymer samples were prepared by compression molding the powders against a "Bonderite" panel (15 × 5 × 0.4 cm) in a press set at 185 ± 5°C. A copper foil was used as the top molding "plate," and following molding, this was removed by amalgamation with freshly distilled Hg. The free polymer surface was then degreased by washing with lint-free paper saturated in pure $CHCl_3$ and finally air dried at 30°C for 24 hr. A number of test panels were aged at 60°C and others at 90°C by storing in ovens which were maintained under a nitrogen atmosphere so as to eliminate the possibility of oxidative changes on the polymer surfaces. The absence of these was confirmed by repetition of intrinsic viscosity measurements, which reproduced initial values to ±5%. Following oven exposure, these aged samples were used to follow γ_c changes, again at the reference temperature of 30°C.

TABLE I
Characterization of Polymers Used in Study

Sample	Composition S/BA/MAA, wt. %	Reduced viscosity,[a] dl/g	M_n,[b] $\times 10^{-4}$	M_w,[b] $\times 10^{-4}$	T_g, °C
1	80/15/5	0.12	1.20	1.77	62
2	80/15/5	0.23	1.96	4.52	62
3	80/15/5	0.38	3.31	15.1	62
4	80/15/5	0.49	3.36	17.3	62
5	84/15/1	0.39	—	—	67
6	70/25/5	0.42	—	—	53

[a] Reduced viscosities measured at 25°C in 95/5 (v/v) ethylene dichloride/ethanol mixtures; polymer concentration, 0.5% (w/v).

[b] Polystyrene-equivalent molecular weights, see Ref. 7.

In earlier tgb work,[1,2] the areas of constant-volume droplets needed for γ_c evaluations were estimated by planimetry. Greater reproducibility is possible by the variation used in this case, as outlined below. A microsyringe of 10 μl capacity was used to place droplets of standard wetting liquids onto the polymer substrate. The standard fluids, all solutions of purified propionic acid in distilled water, had known γ_{LV} values, as determined by du Nuoy ring tensiometry and recorded in Table II.

Preliminary experiments showed that at 30°C these solutions interacted slowly with the polymer films, significant spreading of droplets being detectable after 10–15 min of contact. The interaction may be due to either or both components of the test solution; in the present context, it was desirable to eliminate its effects. Consequently a photograph of deposited droplets was taken at 1-min intervals up to a maximum contact time of 5 min. Prints of the photographs were then used to make photocopies on standard graph paper. Droplet shapes were carefully cut out and weighed, at least two weight determinations being used for each contact time, and an average value $\overline{W}$ for each of the test fluids at zero contact time was then calculated from ~10 data points. Values of $\overline{W}$ normalized to a constant enlargement factor of 5:1 were found to be reproducible to within ±3%. An illustration of five droplets on a S/BA/MAA = 80/15/5 substrate (5-min contact time) is shown in Figure 1. As in previous work,[1,2] $\overline{W}$ was plotted against

TABLE II
Composition and γ_{LV} of Test Fluids

Fluid	Propionic acid, g/100 ml	γ_{LV}, dyn cm^{-1}
1	1.910	60.2
2	5.838	49.2
3	9.804	44.0
4	13.002	40.9
5	21.705	35.8
6	30.115	33.5
7	50.001	31.5

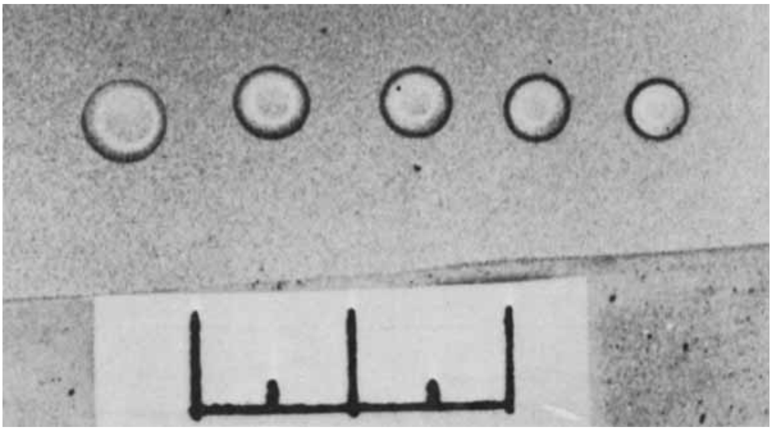

Fig. 1. Droplets of propionic acid solutions on S/BA/MAA polymer film at 30°C; note 2-cm scale marking.

γ_{LV}, producing well-defined linear relationships (Fig. 2). The key to determining γ_c is the construction of a horizontal line representing W_{lim}, the limiting weight of a circle produced by a liquid having 0° contact angle with the substrate. Theoretically, W_{lim} would be defined by the circle corresponding to a droplet forming a monolayer on the solid; that is, $\overline{W}$ must increase nonlinearly as this condition is approached. Empirically, however, we have found that W_{lim} may be obtained to within an error of ±3% by applying droplets of the test fluids to calibrated standard substrates, the values for which were measured by the Zisman contact angle method. These solids were as follows:

Linear polyethylene: $\gamma_c = 30.7 \pm 0.5$ dyn cm^{-1}
Polystyrene: $\gamma_c = 34.5 \pm 0.5$ dyn cm^{-1}
"Mylar": $\gamma_c = 42.2 \pm 0.5$ dyn cm^{-1}

Each of these polymers defined the same limiting value, $W_{\text{lim}} = 0.514$ (g) ± 0.008. Adopting this parameter in further analysis, values of γ_c for the experimental polymers were determined with a precision of about 3%, as shown in Figure 2 for samples 3 and 6 of Table I. The reference values of γ_c (that is, prior

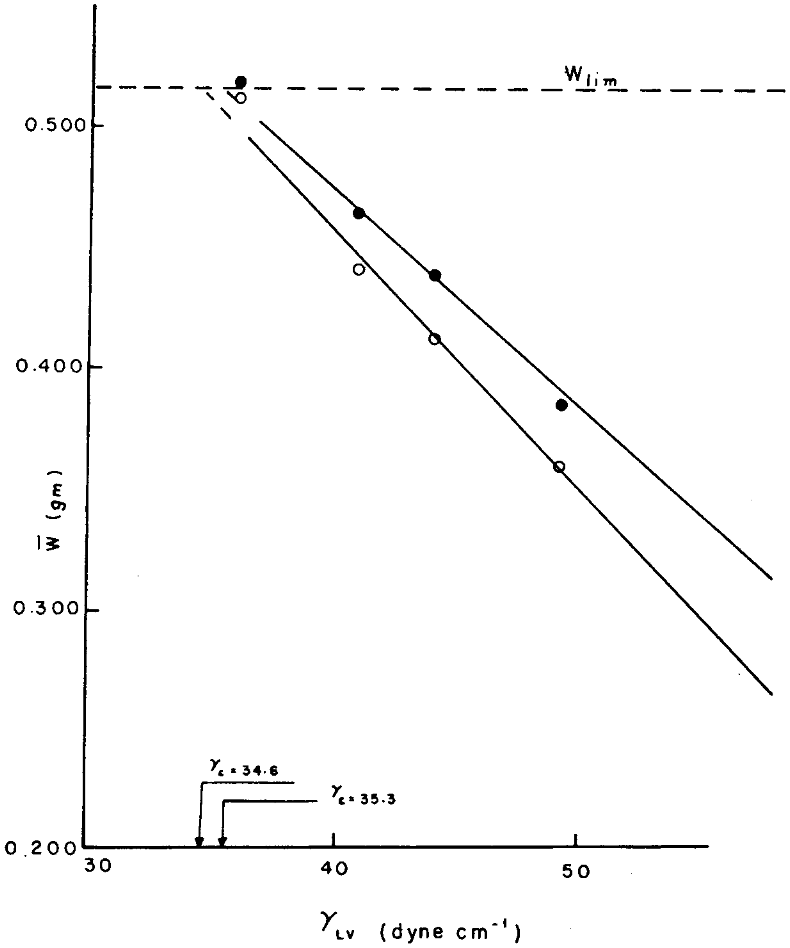

Fig. 2. Illustration of γ_c determination from droplet weight measurements: ●, 70/25/5 polymer (sample 6); ○, 80/15/5 polymer (sample 3).

to high-temperature aging of the samples) are as follows:

80/15/5 series = 34.5 (± 0.7) dyn cm^{-1}
70/25/5 series = 35.3 (± 0.7) dyn cm^{-1}
84/15/1 series = 33.8 (± 0.8) dyn cm^{-1}

Since the γ_c values for samples 1–4 were within the 3% experimental error, only one datum is used to represent this series of polymers. The datum is in very good agreement with previous evaluations,[2] in which planimetric measurements of droplet surface area were used to estimate the surface tension. It is evident that the γ_c values of these polymers are dominated by the low-surface-energy component of the material. Indeed, in the case of samples 1–5, the γ_c values are essentially those of polystyrene, the contribution of the acrylic component—expected[8] to be in the range 40–44 dyn cm^{-1}—becoming evident only in sample 6, though to a lesser extent than expected on the basis of stoichiometry.

RESULTS AND DISCUSSION

In this section emphasis is placed on the use of γ_c data as an analytic tool for the detection of surface changes due to high-temperature exposure of the test films. The suitability of this experimental approach is clearly demonstrated in Figure 3, in which γ_c variations for the 80/15/5 polymer series resulting from aging at 60 and 90°C is documented. Only one set of data points is given for 60°C exposure, no detectable difference having been found among samples 1–4. Thus while an experimentally significant rise in γ_c toward 36.5 dyn cm^{-1} is observed within the maximum exposure time of ~500 hr, this increase seems not to depend on the molecular weight of the materials. Aging at 90°C—some 30°C in excess of the T_g for the polymers—produces not only an accelerated and sharper rise in γ_c, but one which is now distinctly more pronounced at higher molecular weights.

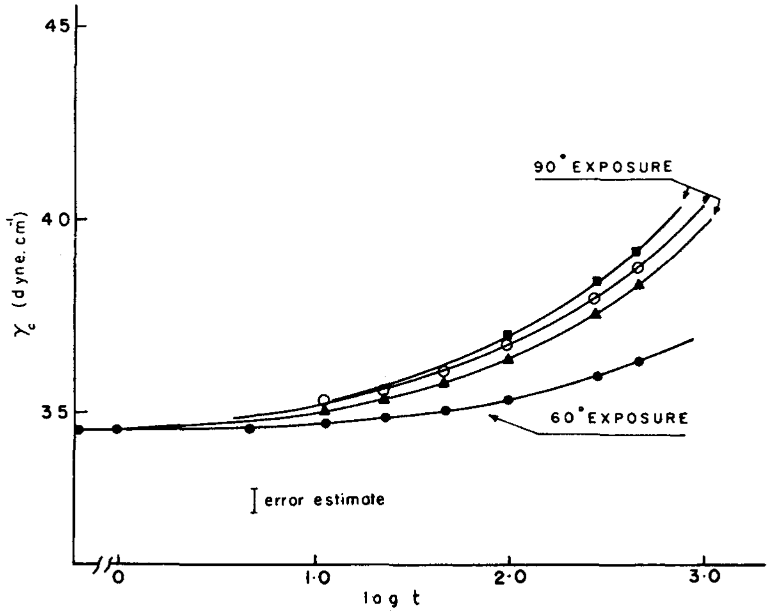

Fig. 3. Time/temperature effect on γ_c of 80/15/5 polymers. Code for 90°C exposure: ■, sample 4; ○, sample 3; ▲, sample 1.

A comparison of the surface property changes in the three polymer structures represented in this work is given in Figure 4. Here samples 3, 5, and 6, all at approximately constant inherent viscosity (i.e., apparent molecular weight), are involved. Again, aging up to ~500 hr at 90°C produces significant increases in γ_c, these being particularly evident in the polymers with high acrylic content. The γ_c change for sample 5 (~1.5 dyn cm^{-1}) is much less pronounced but still significant. The high-temperature aging effect is therefore promoted by higher molecular weight and by the increased content of the acrylic components.

The inference in the given results, i.e., that surface property changes occur more rapidly at $T > T_g$ of the polymers, is confirmed by the results in Figure 5. Samples 1, 3, 5, and 6 represent the three polymer groups, and the data were obtained from tgb experiments in the temperature range 35–82°C. Samples were aged on the gradient bar for several hours, γ_c of the polymers being determined systematically at 30°C following fixed aging times at the indicated temperatures. The data in Figure 5, typical of the results obtained, display the change in critical surface tension after 8-hr aging; the parameter $\Delta\gamma_c$ is defined as $\Delta\gamma = (\gamma_t - \gamma_0)$, where γ_t is the surface tension after the polymer was aged for time t and γ_0 is the initial value of γ_c. Clearly, significant increases in γ_c occur in each case when aging occurs at $T > T_g$. For the 70/25/5 series (sample 6) this occurs above ~50°C, consistent with the T_g of this material (see Table I). At the other extreme, sample 5, representing the 84/15/1 series, shows significant $\Delta\gamma_c$ above ~65°C, again consistent with its higher T_g value. The inferences of these data are to the effect that a diffusion-controlled mechanism produces an apparent enrichment of acrylic content in the surfaces of these polymers, the importance of this enrichment effect varying directly with overall acrylic content in the polymer and with molecular weight.

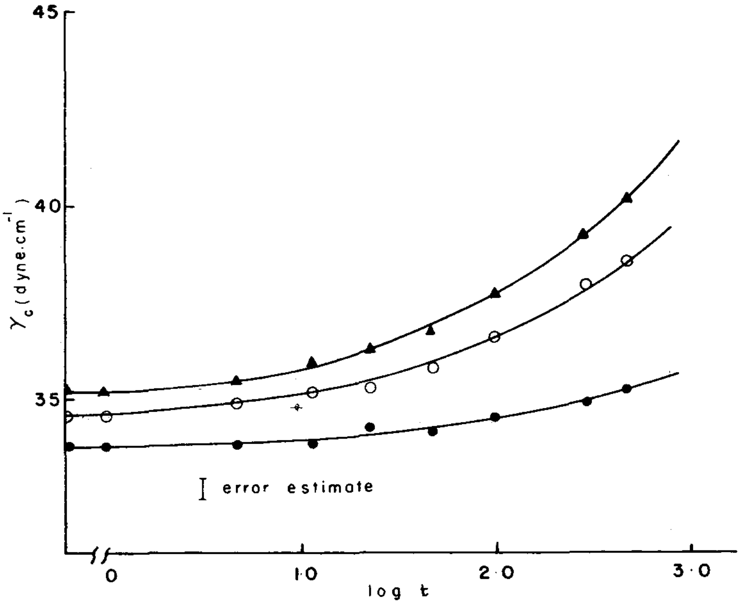

Fig. 4. Comparison of γ_c changes due to exposure at 90°C: ▲, 70/25/5 polymer; ○, 80/15/5; ●, 84/15/1.

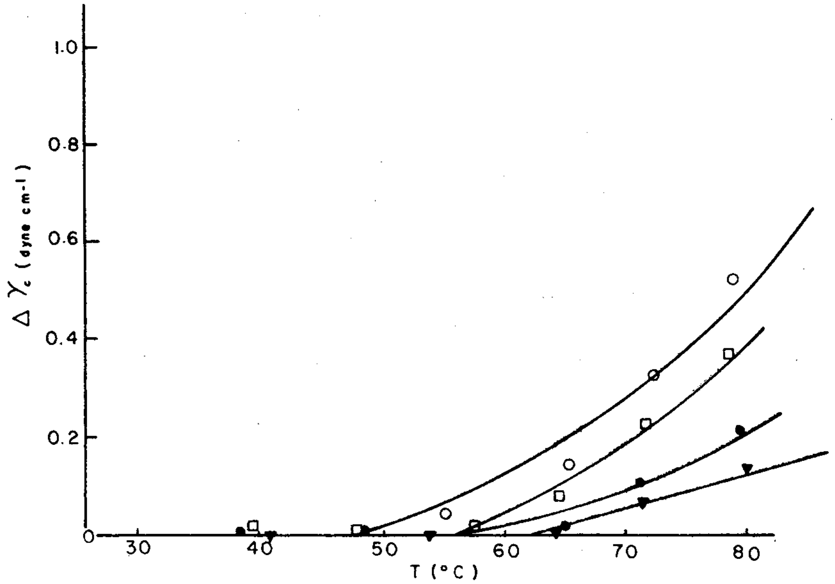

Fig. 5. $\Delta\gamma_c$ due to isochronous aging at temperatures to 80°C: ○, 70/25/5 polymer; □, 80/15/5 polymer, sample 3; ●, 90/15/5 polymer, sample 1; ▼, 84/15/1 polymer.

NATURE OF AGING EFFECT

The data in hand do not permit a resolution of the mechanism(s) responsible for the observed aging effects. Thermal instability may be ruled out, earlier work with the 80/15/5 series having shown these polymers to be stable for many hours at temperatures well above those involved here.[7] An increase in γ_c toward some equilibrium value higher than the initial measurement is not consistent with the thermodynamic behavior of miscible systems. It is likely therefore that the present polymer systems are multiconstituent in nature and that included in them are immiscible moieties, richer in acrylic content. These may gradually migrate to the interfaces, the increase in γ_c at the air interface being offset by the overall decrease in the bulk free energy of the system on demixing. The known, broad molecular weight distribution in these polymers[7] is qualitatively consistent with this suggestion. Further, the polymers were prepared by a proprietary process in which it is probable that the methacrylic acid serves as a particle stabilizer. It may, therefore, be sorbed by the polymer particles, remain there as a low-molecular-weight moiety and thus be the species alluded to above. An alternative suggestion consistent with the observations is based on recently published results of gas chromatographic experiments,[9] which showed that the initial chain orientation of poly(methyl methacrylate) at solid–gas interfaces depended strongly on the solvent from which the polymer film was formed and changed slowly on subsequent thermal aging of the polymer. These conclusions were drawn from the behavior of specific retention volumes for various probe gases in contact with the polymer surfaces; analogously, it may be argued that thermally induced chain orientation effects in the present acrylic copolymers favor an apparent surface enrichment of the polar groups, giving the overall impression of nonisotropy. Additional experiments will be required to discuss this matter more fully.

In any event, the practical consequences of these surface property changes should be important, since presumably, such characteristics of coatings produced from the polymers as intercoat adhesion, wettability, etc., should respond to aging effects in a manner consistent with the structural changes attributed to it. Indeed, experimentally significant temperature and time-dependent changes in the bond strength of joints using these polymers as adhesives have been observed, and they will be discussed in a separate publication.

The allegation of diffusion-dominated mechanisms for surface property changes, made above, is more readily tested through an application of the theory for diffusion mechanisms. If migrating acrylic-rich polymer chains are regarded as solvents in the overall polymer structure, then well-known theory[10–12] may be applied to the set of γ_c, T, and t data. Thus if γ_0 is the initial surface tension datum, characterizing some starting apparent concentration of acrylic moieties in the surface, then $(\Delta\gamma_c)_t$ is associated with a finite increase in that effective concentration at time t. Following standard procedures,[10–12] we then write:

$$(\Delta\gamma_c)_t = (\Delta\gamma_c)_\infty \frac{2}{l}\left[\left(\frac{Dt^{1/2}}{\pi}\right)\right] \tag{1}$$

where $(\Delta\gamma_c)_\infty$ is the final steady-state value, l is the half-thickness of the polymer film, and D is the diffusion coefficient for the process, which has a value in the range 10^{-8}–10^{-9} cm^2 sec^{-1}. In accordance with eq. (2), a plot of $(\Delta\gamma_c)_t$ versus $t^{1/2}$ should be linear and pass through the origin. Figures 6 and 7 represent a test of this concept, the former giving data at 60°C, the latter at 90°C. In both cases substantial linear segments support the diffusion mechanism, though only the 84/15/1 specimens satisfy the condition of linearity passing through the origin. The polymers with greater acrylic content appear to have "induction times," these being of the order of 20 hr at 60°C and about 2–5 hr at 90°C. As before,

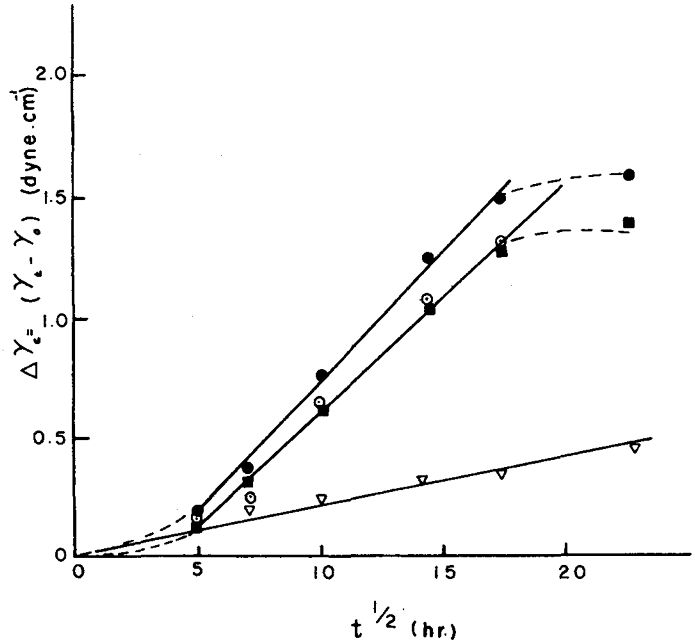

Fig. 6. Time dependence of γ_c for 60°C exposure: ●, 70/25/5 polymer; ■, 80/15/5 polymer, sample 3; ○, 80/15/5 polymer, sample 1; ▽, 84/15/1 polymer.

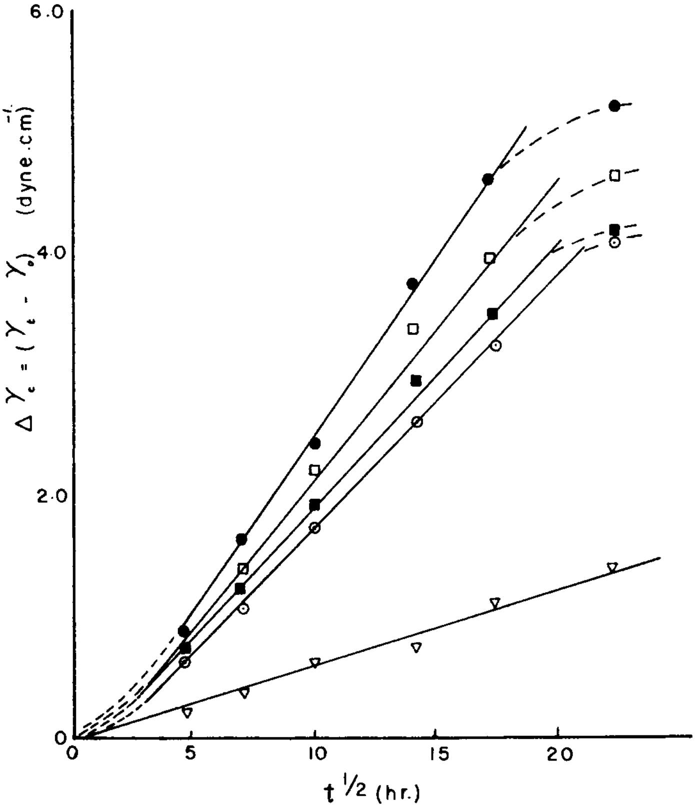

Fig. 7. Time dependence of γ_c for 90°C exposure: ●, 70/25/5 polymer; □, 80/15/5 polymer, sample 4; ■, 80/15/5 polymer, sample 3; ○, 80/15/5 polymer, sample 1; ▽, 84/15/1 polymer.

at 60°C no molecular weight effect is to be seen in the 80/15/5 sequence, the matter being different at the higher temperature. At both temperatures, deviation from linearity occurs as expected at long times. Presumably this indicates a close approach to or attainment of equilibrium surface conditions. Qualitatively the present diffusion-controlled changes in the surface states (γ_c) of these polymers are consistent with the findings of Lee[13]; the high value of the diffusion coefficient favors the idea that the diffusing species are oligomeric, the diffusion coefficients for many polymers being several orders of magnitude smaller.[13] Present γ_c data also follow patterns similar to those reported recently by Chang and Gray[14] for hydroxypropyl cellulose. In the latter case, time-dependent nucleation and crystallization phenomena were responsible for major surface tension variations. As already noted, the data available to us do not permit a resolution of the possibilities offered above; their fundamental and practical inferences, however, indicate the need for further analysis of the root causes for the phenomena discussed here.

CONCLUSIONS

The present paper gives initial evidence that monitoring critical surface tension data is an informative guide to surface property changes induced by time/temperature cycles in a series of styrene–acrylic film-forming polymers. A thermal gradient bar is a particularly convenient tool for such monitoring procedures. A diffusion-controlled mechanism (or mechanisms) seems to be responsible for an effective increase in the surface concentration of acrylic content, leading to a systematic rise in the critical surface tension of the polymers from initial values in the range 34–35 dyn cm^{-1}, typical of styrene polymers, to values in the 38–40 dyn cm^{-1} range, which is consistent with the surface tensions of predominantly acrylic polymers. The effect, suggesting the migration of immiscible moieties to the interface, is of increasing importance in polymers with high overall acrylic content and is also accentuated at higher molecular weight. Further study is in progress to clarify the processes involved and to outline their practical consequences in the performance of these polymers as coatings or adhesives.

We thank the Paints Division, Canadian Industries Ltd., Toronto for their support of this work. Financial aid from the National Research Council of Canada is gratefully acknowledged.

References

1. F. Ewane-Ebele and H. P. Schreiber, *J. Oil Col. Chem. Assoc.*, **60**, 249 (1977).
2. H. P. Schreiber and F. Ewane-Ebele, *Adhesion,* **9**, 175 (1978).
3. C. Huh and S. G. Mason, *J. Colloid Interface Sci.*, **60**, 11 (1977).
4. J. F. Oliver and S. G. Mason, *J. Colloid Interface Sci.*, **60**, 480 (1977).
5. H. W. Fox and W. A. Zisman, *J. Colloid Sci.*, **7**, 109 (1952).
6. A. W. Newman, *Adv. Colloid Interface Sci.*, **4**, 105 (1974).
7. H. P. Schreiber and G. J. Thibault, *J. Coat. Technol.*, **50**, 56 (1978).
8. L. H. Lee, "Interaction of Liquids at Solid Substrates," Chap. 8, in *Adv. Chem. Ser.*, **87**, American Chemical Society, Washington, D.C., 1968.
9. M. Croucher and H. P. Schreiber, *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 1269 (1979).
10. J. Crank, *The Mathematics of Diffusion,* Clarendon Press, Oxford, 1956.
11. R. M. Vasenin, *Vysokmol. Soedin.*, **6**, 624, 1700 (1964).
12. E. Southern and A. G. Thomas, *Trans. Faraday Soc.*, **63**, 1913 (1967).
13. L. H. Lee, *J. Polym. Sci., Part A2* **5**, 751 (1967).
14. S. A. Chang and D. G. Gray, *J. Colloid Interface Sci.*, **67**, 255 (1978).

Received April 25, 1979
Revised June 4, 1979