TABLE I
BULK COPOLYMERIZATION OF STYRENE AND ACRYLONITRILE (AN) IN THE ABSENCE OR PRESENCE OF $ZnCl_2$ AND/OR BENZOYL PEROXIDE (BP) AT 60°

AN in feed, mole %	$ZnCl_2$/AN, mole ratio	BP, mole % (on AN + S)	Time, min	Yield, %	[η], dl/g	N, %	AN in copolymer, mole %
25	0	0.2	30	2.5	0.88	4.67	29.5
50	0	0.2	30	2.1	0.68	6.60	39.5
75	0	0.2	30	5.5	1.30	8.68	49.5
25	0.1	0	40	3.6	2.50	8.72	49.5
50	0.1	0	30	2.8	2.20	8.72	49.5
75	0.1	0	40	6.2	2.08	8.80	50.0
25	0.1	0.2	5	1.8	2.89	8.70	49.5
50	0.1	0.2	5	5.8	1.33	8.71	49.5
75	0.1	0.2	5	5.8	1.60	9.10	50.5

TABLE II
BULK COPOLYMERIZATION OF STYRENE AND ACRYLONITRILE (AN) IN THE ABSENCE OR PRESENCE OF $ZnCl_2$ AND/OR *t*-BUTYL PEROXYPIVALATE (TBPP) AT 25°

AN in feed, mole %	$ZnCl_2$/AN, mole ratio	TBPP, mole % (on AN + S)	Time, min	Yield, %	[η], dl/g	N, %	AN in copolymer, mole %
25	0	1.0	150	2.4	0.82	5.25	32.6
50	0	1.0	150	2.9	1.10	7.10	42.0
75	0	1.0	150	2.9	1.01	9.15	51.5
25	0.1	0	150	0			
50	0.1	0	150	0			
75	0.1	0	150	0			
25	0.1	1.0	35	7.8	5.34	7.98	46.3
50	0.1	1.0	35	10.0	5.13	8.51	48.5
75	0.1	1.0	35	8.1	3.68	8.77	50.0

$ZnCl_2$:AN ratio is increased from 1:10 to 1:2. Similar results have been noted in the styrene–methyl methacrylate–$Et_{1.5}AlCl_{1.5}$ systems.[9]

The influence of temperature on the bulk copolymerization is shown in Table II. Little or no polymer is obtained at 25° after 150 min in the presence of zinc chloride and the absence of a radical catalyst. Thus, the rate of spontaneous homopolymerization of the S–AN · · · $ZnCl_2$ complex is negligible at 25° as compared to 60°.

The radical catalyst, *t*-butyl peroxypivalate, alone in the absence of zinc chloride yields a low molecular weight copolymer whose composition is that of a conventional radical copolymer. Although higher molecular weight copolymer would be expected at 25° than at 60°, the fivefold greater catalyst concentration at 25° is reflected in the similarity of the molecular weights at the two temperatures. However, the presence of zinc chloride and the radical catalyst at 25° yields extremely high molecular weight, essentially 1:1 copolymers, at styrene–acrylonitrile molar ratios of 3:1, 1:1, and 1:3.

The styrene–acrylonitrile · · · $ZnCl_2$ system gives similar results in toluene as in bulk at 60°. However, the use of ethyl acetate as reaction medium inhibits or prevents the polymerization, probably due to complexation with $ZnCl_2$ in competition with acrylonitrile.

The copolymerizations were carried out with distilled monomers in a three-necked round-bottomed flask with magnetic stirring. The zinc chloride was heated for 3 hr at 220° under vacuum before use and mixed with acrylonitrile and styrene at 25 or 60° under a nitrogen atmosphere. The radical catalyst, where used, was then added. The originally homogeneous mixture became heterogeneous as polymerization proceeded due to precipitation of the copolymer. After the desired reaction period, acetone was added to terminate the reaction and dissolve the copolymer. The latter was precipitated by pouring the solution into methanol, filtered, and dried *in vacuo* at 40°.

Copolymer composition was determined by elemental analyses. Intrinsic viscosities were measured in dimethylformamide at 30° in a Ubbelohde viscometer.

(9) N. G. Gaylord and H. Antropiusova, *J. Polym. Sci., Part B*, 7, 145 (1969).

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Estimation of Glass Transition Temperatures from Gas Chromatographic Studies on Polymers

In a recent communication, Smidsrød and Guillet[1] showed that thermodynamic data on the interactions between polyisopropyl acrylamide and various gaseous solutes could be obtained by making the polymer the stationary phase in a gas chromatograph. It was also shown that if a solute was used which was a nonsolvent for the polymer, a plot of the logarithm of the specific

(1) O. Smidsrød and J. E. Guillet, *Macromolecules*, in press.

TABLE I
Summary of Data Derived from Retention Diagrams

Polymer substrate	Polyvinyl chloride (A)	Polyvinyl chloride (B)	Polystyrene	Poly mMA
Mol wt (M_n)	68,000	35,500	51,000	48,000
Column loading, g	0.227	0.116	0.088	0.357
Solute	*n*-Dodecane	*n*-Dodecane	*n*-Dodecane	*n*-Hexadecane
D.S.C. glass transition, °C	75 ± 2	75 ± 2	95 ± 2	100 ± 2
Temp of first deviation from linear relation, T_1, °C	81	81	88	97
Temp of curve min., T_2, °C	91	91	100	105
Enthalpy of adsorption ΔH_a, kcal mol^{-1}	−1.2	−1.3	−2.7	[a]
Enthalpy of mixing ΔH_m, kcal mol^{-1}	+3.8	+3.8	+2.5	+4.4

[a] Vapor pressure data on *n*-hexadecane not available in this temperature range.

retention volume as a function of reciprocal temperature showed a marked inflection at a temperature close to the glass transition temperature for the polymer. We wish to report similar data on several additional polymers which lead us to believe that the phenomenon is a general one and may be used to obtain an estimate of transition temperatures for a variety of polymeric materials.

The polymers used were obtained from the following sources: (a) polymethyl methacrylate, Fisher Laboratory Chemical (Fisher Scientific Company), $\overline{M}_n$ = 48,000; (b) polystyrene, narrow distribution polymer obtained from Pressure Chemical Company, Pittsburgh, Pa., lot No. 7a, $\overline{M}_n$ = 51,000, $\overline{M}_w/\overline{M}_n$ = 1.06; (c) polyvinyl chloride, samples courtesy of Imperial Oil Enterprises Ltd., Sarnia, Ont., Canada, approximate number average mol wt, sample A, 68,000; sample B, 35,500.

The polymers were dissolved in a suitable solvent and deposited on the surface of Chromosorb G by gentle stirring in a stream of dry nitrogen to evaporate the solvent. The concentration of the polymer on the absorbent was determined by gravimetric analysis before and after the coating and drying procedure. The samples were dried in a vacuum oven for 2 hr and then packed into 1/8 in. diameter columns 5 ft in length. The gas chromatograph used was a Perkin-Elmer Model 800 with dual flame ionization detectors. Nitrogen was used as the carrier gas and measurements were made of the flow rate and pressure drop across the column at the various temperatures. The temperature of the oven was calibrated using a standard thermometer. The column temperatures were constant to within ±0.3°. Glass transition temperatures were measured using a Perkin-Elmer DSC1B differential scanning calorimeter. The glass transition temperature, T_g, was taken to be the temperature at which the base line first deviated from the level position. The values reported are the average of five determinations.

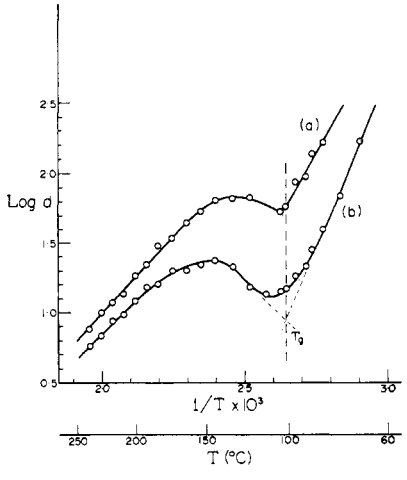

Figure 1. Retention times for *n*-hexadecane on polymethyl methacrylate column (0.357 g on Chromosorb W). Times measured in arbitrary units (mm chart distance). Nitrogen flow rate 0.496 cc sec^{-1}.

The four polymers used in this work were polymethyl methacrylate, polyvinyl chloride (two samples of different $\overline{M}_n$), and polystyrene. The solutes used were *n*-dodecane (Fisher Scientific Company, purified) and *n*-hexadecane (J. T. Baker Chemical Co., purified). In a typical experiment the column would be allowed to equilibrate for about 5 min to reach temperature equilibrium and then from five to ten injections of the solute would be made in amounts varying from about 1 μl. A small amount of methane was usually included in the sample to mark the position corresponding to no adsorption. The retention volume was determined from the distance between the methane peak and the peak maximum for the particular solute used. This would then be plotted as a function of concentration and extrapolated to infinite dillution. It was found that in most cases there was no change in the retention time or volume for samples below 0.01 μl and consequently an average value for specimens of 0.01 μl or less could be used to determine the value of V_g.

The simplest method of plotting the data is shown in Figure 1 in which the distance between the two peaks, *d*, as measured from the chart paper is plotted on a logarithmic scale as a function of reciprocal of the absolute temperature for a sample of polymethyl methacrylate (curve a). Another method is obtained by plotting *d'*, the distance from the methane peak to the front of the solute peak (curve b), a procedure recommended by Cruickshank, *et al.*,[2] for obtaining thermodynamic data. In both cases a sharp transition is obtained at a temperature close to that of the glass transition.

More significant information can be obtained from data, however, if instead of plotting peak distances or

(2) A. J. B. Cruickshank, D. H. Everett, and M. T. Westaway, *Trans. Faraday Soc.*, **61**, 235 (1965).

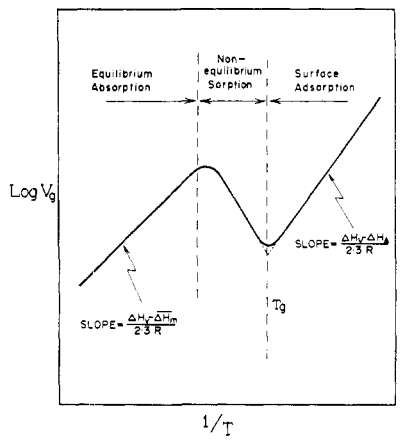

Figure 2. Generalized retention diagram for "nonsolvent" vapor components on glassy polymer substrates.

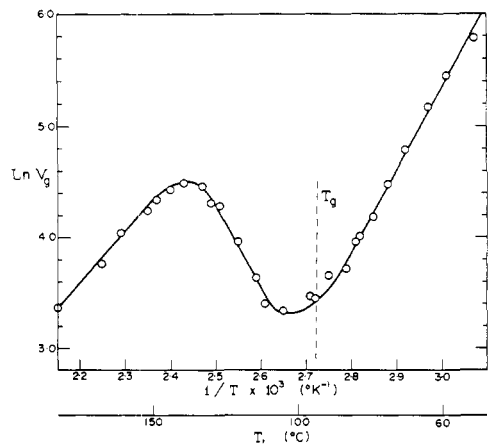

Figure 3. Retention diagram for *n*-dodecane on polystyrene column. Nitrogen flow rate 0.496 cc sec^{-1}.

peak times the data are converted to retention volumes by the procedure described by Purnell[3] and the logarithm of the specific retention volumes plotted versus reciprocal temperature. Such plots have the shape shown in Figure 2. From the slopes of the low- and high-temperature portions of the curve, one can also estimate the heat of adsorption of the solute on the polymer surface and the heat of mixing for the solute with the polymer solvent respectively. Data of this kind are plotted for polystyrene in Figure 3, and two samples of differing molecular weight of polyvinyl chloride in Figure 4. In each case the presence of a sharp inflection in the curve at or near the glass transition temperature is quite evident. Results for the determination of the glass transition temperature using the differential scanning calorimeter for the same polymers are shown in Figure 5.

Data on the heats of adsorption, ΔH_a, and mixing, ΔH_m, calculated from these curves are shown in Table I.

These results seem to confirm the mechanism proposed by Smidsrød and Guillet[1] for the phenomenon. At low temperatures, below the glass transition only a small retention of the solute is obtained due presumably to a monomolecular adsorption on the surface of the

(3) J. H. Purnell, "Gas Chromatography," John Wiley & Sons, Inc., New York, N. Y., 1962.

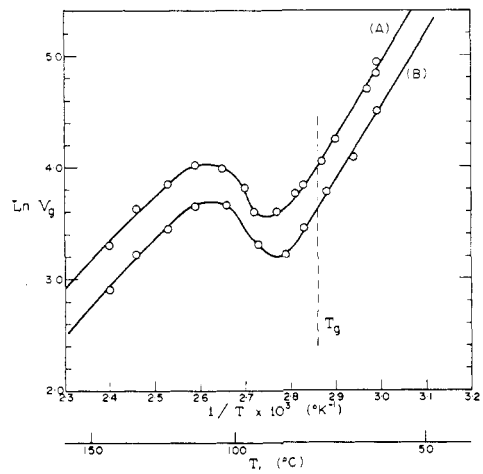

Figure 4. Retention diagram for *n*-dodecane on polyvinyl chloride columns. Nitrogen flow rate 0.496 cc sec^{-1}.

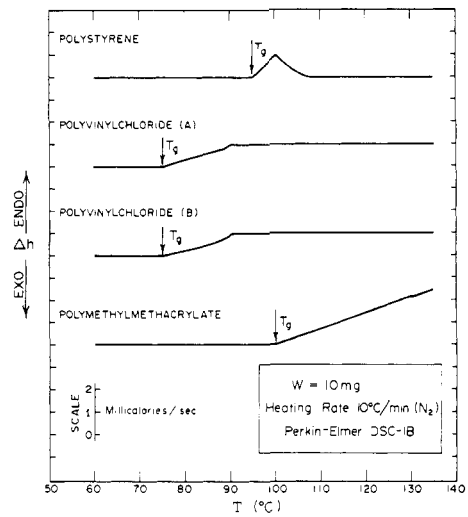

Figure 5. Differential thermograms for various polymers.

polymer film. The relatively small value of the heat of adsorption of around 1 kcal/mol would be consistent with the relatively weak van der Waals attractive forces which might be expected to exist between a hydrocarbon molecule and a relatively polar polymer. Below the glass transition temperature, the segmental motion is too slow to permit the penetration of the relatively large solute molecule. Further, the elements of free volume in the system must be too small to allow the penetration of these molecules into the bulk of the polymer film. Consequently there is no solution of the solute molecule below the glass transition. At the glass transition temperature and above, the free volume of the system becomes such that solute molecules begin to penetrate the polymer matrix and the increase in penetrability more than counteracts the increase in vapor pressure of the solute so that an inversion of the usual temperature coefficient of the retention volume occurs and retention time increases as the temperature increases. At some higher temperature, diffusion of the solute in the polymer becomes sufficiently rapid so that equilibrium can be established during the time of passage of the solute peak through the column. At all temperatures above this point, the normal gas-chroma-

tographic behavior is obtained and the retention time and volume will decrease with increasing temperature. From the slope of this upper part of the curve one can estimate the heat of mixing of the solute in the polymer phase. One may also of course estimate other thermodynamic quantities from this portion of the curves as was done by Smidsrød and Guillet for polyisopropyl acrylamide with various solutes. However, there is still some question about the thermodynamic interpretation of these data and hence we have not reported them in this communication. The positive heat of mixing obtained in these experiments is approximately 3 kcal/mol and is of the order of magnitude which might be expected for systems of this type.

Since the phenomenon appears to be quite general, we suggest that this method may well prove to be a reliable procedure for estimating glass transition temperatures in polymers either to supplement or to replace thermal measurements. Since one can quite easily vary the size of the penetrating solute molecule, the possibility exists that one may obtain a measure of the free volume available in the polymer at temperatures above T_g or from the value of T_g itself as it may vary with the size of the penetrating molecule. Further applications of the technique will be discussed in a later communication.

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Dielectric Properties of Polypropylene Oxide as a Function of Concentration

In a recent publication Baur and Stockmayer[1] discussed the dielectric properties of polypropylene oxide of molecular weight 2025. In particular they identified

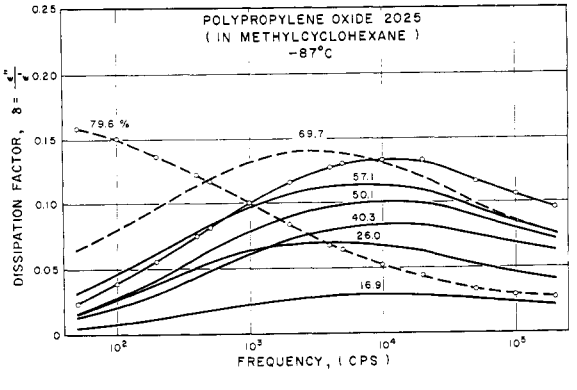

Figure1.

(1) M. E. Baur and W. H. Stockmayer, *J. Chem. Phys.*, **43**, 4319 (1965).

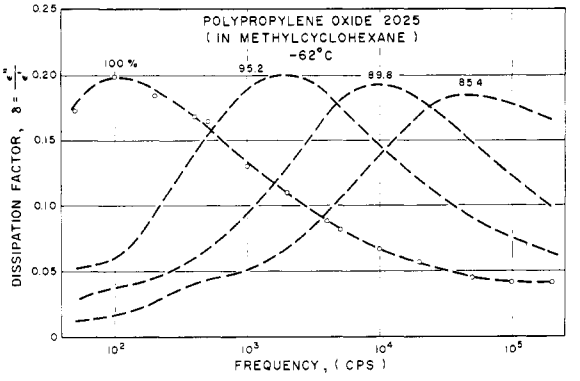

Figure 2.

a very strong dispersion region associated with a dipole moment perpendicular to the chain contour and whose frequency ν_m at which maximum loss occurred was independent of molecular weight. At $-35°$ ν_m for this dispersion was 2×10^5 cps.

We thought that it would be interesting to study ν_m as a function of polymer concentration in a nonpolar solvent, methylcyclohexane.

We found an interesting result: ν_m was dependent on polymer concentration between 65 and 100 wt % of polymer. At concentrations below 65 wt % of polymer, ν_m was nearly independent of polymer concentration.

We used a similar bridge as in ref 1. Measurements could be made between 50 and 2×10^5 cps. In order to broaden the frequency scale we made measurements at different temperatures and used the time–temperature superposition principle in the same manner as in ref 1. Measurements were made at -89, -78, -62, -33, and 25°.

Some of the results are presented in Tables I and II and in Figures 1–3. Figure 1 shows experimental data at $-87°$, Figure 2 shows experimental data at $-62°$, and Figure 3 shows temperature–frequency superposed data (from numerous temperatures) reduced to $-33°$. The figures show the dissipation factor $\delta = \epsilon''/\epsilon'$ plotted against log ν. The tables show ν_m, δ_m (measured at ν_m), the logarithmic half width of the dispersion region, and the viscosity η of the solutions, all data reduced to $-33°$.

If the damping were related to solution viscosity, the

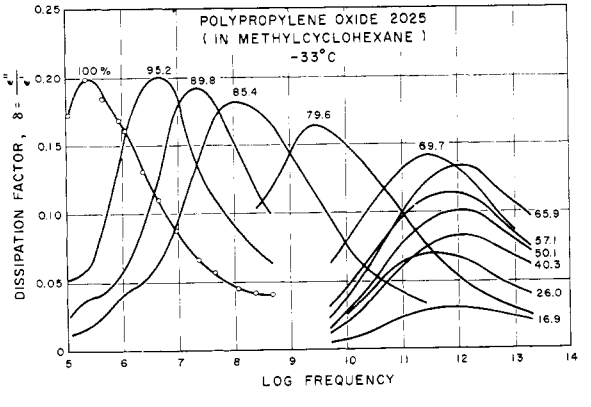

Figure 3.