The Solubility of Poly(vinylidene Chloride)

RITCHIE A. WESSLING, *Polymer Science Physical Research Laboratory,
The Dow Chemical Company, Midland, Michigan 48640*

Synopsis

The relative abilities of various solvents to dissolve crystalline polyvinylidene chloride
were judged by comparing temperatures at which dilute suspensions became homo-
geneous. PVDC is not soluble in common solvents at ambient temperatures. It dis-
solves in solvents of matching solubility parameter only above ~130°C. An analysis
of the data suggests that $\delta = 10.1$ for PVDC. Five classes of specific solvents were
observed that could dissolve PVDC at much lower temperatures. These include sulfox-
ides, dialkyl amides, alkyl lactams, cyclic sulfides, and cyclic ketones. PVDC acts as
a weak Lewis acid in these solutions. The best solvents found, in order of decreasing
activity, are: hexamethylphosphoramide, tetramethylene sulfoxide, N-acetylpiperi-
dine, N-methylpyrrolidone, N-formylhexamethyleneimine, and trimethylene sulfide.

INTRODUCTION

An investigation of the solubility of poly(vinylidene chloride) (PVDC)
was undertaken in order to find solvents for dilute solution and crystalliza-
tion studies. The characterization of this polymer has been limited both
by its thermal instability and its apparent insolubility in common solvents.
Thus, even though PVDC has been known since the early days of polymer
science,[1] its behavior in solution has not been investigated nor have any
quantitative molecular weight measurements ever been reported. Prob-
ably as a result, studies of the crystalline state in this polymer have been
limited.[2] However, because of its high crystallinity and simple structure, a
thorough investigation of the solid state properties of PVDC could con-
tribute significantly to our general understanding of crystalline polymers.

A standard method for predicting polymer solubility is by the use of
solubility parameters. Burrell[3] estimated a value of $\delta = 12.2$ for PVDC.
Measured values on copolymers, however, range from 9.5 to 14.7.[4]

We can calculate δ from existing data using Small's method[5]:

$$\delta = \frac{d\sum G_i}{M}$$

where d is density, G_i is a molar attraction constant, and M is the molecular
weight. The density of PVDC in the amorphous state is difficult to
measure directly. The older value of 1.66 g/cc gives $\delta = 9.6$.[6] A more
recent estimate[7] of 1.7754 g/cc gives $\delta = 10.2$. Both values are significantly
lower than Burrell's estimate.

The problem may lie in the fact that crystallinity interferes with conventional techniques for obtaining solubility parameter data. Highly crystalline polymers swell erratically and normally dissolve only at temperatures near their melting points. The solubility at lower temperatures is not due to unfavorable polymer–solvent interactions. Rather, it is because most solvents cannot interact strongly enough to depress the melting point of the mixture. This must be true for all regular polymer solutions, i.e., for which $\Delta H_M > 0$, $\Delta S_M{}^E = 0$, and $\Delta V_M = 0$.[8] And it is only in these solutions that the solubility parameter concept applies. There is no theory which can predict the behavior of polymers forming nonregular solutions.[9]

In solutions of nonpolar polymers, strong interactions are not possible. We need only to match solubility parameters while minimizing the molar volume to find the best solvent. This follows directly from Flory's theory of melting point depression[10] expressed as

$$\frac{1}{T_M} - \frac{1}{T_M{}^0} = \frac{RV_u}{\Delta H_u V_1} (v_1 - \chi_1 v_1{}^2) \tag{1}$$

If χ_1, the interaction parameter, is zero, T_M depends only on V_1 for a given composition. However, V_1 can be reduced only so far before the boiling point of the solvent at atmospheric pressure is lower than the solution temperature. At the other extreme are polymers with known specific interactions such as hydrogen bonding polymers, polyacids, and polybases. Normally, a solvent which can satisfy these secondary bonding requirements will dissolve the polymer. Melting point depressions in these cases can be very large.

Intermediate cases such as PVDC are difficult to analyze. Often very specific dipolar interactions are found which are unique to a particular class of solvents. Sometimes, this behavior can be deduced from a study of mixtures of low molecular weight components with similar structural features. Small[5] has analyzed the solubility behavior of poly(vinyl chloride) (PVC) in detail using such methods. The results can be correlated by assuming that PVC is a weak electron acceptor and interacts strongly with electron-donating solvents, such as ketones, ethers, esters, etc. A more recent study by Adelman and Klein[11] supports this view and sheds additional light on the specificity of the interactions.

A similar analysis of the behavior of PVDC should be possible. Such materials as hot tetrahydrofuran, dimethyl acetamide, and cyclohexanone are considered to be good solvents.[12] The patent literature reveals a variety of other polar solvents which are supposed to be more effective, but no quantitative measures of solubility are reported.[13-16] Solvents suggested in these patents include sulfoxides, sulfones, sulfonamides, dialkylamides, tetraalkylphosphonamides, hexamethylphosporamide, and alkylpyrrolidones. Interestingly, many of these same solvents dissolve polyacrylonitrile and PVC as well. This suggests that, like these polymers, PVDC is a weak Lewis acid. It differs from them however in being much more crys-

talline.   Therefore, the analysis of PVDC solubility behavior in terms of melting point depression theory is more feasible.

EXPERIMENTAL

Solution Temperature Measurements

The polymers used in the solution temperature measurements were prepared in emulsion by a technique similar to that described by Woodford.[17] The polymers were isolated by freeze-coagulation, washed free of soap, and dried to constant weight in vacuo at 30°C.   Conversions based on monomer charged were above 90% in all runs.

The dried solids were ground to a fine powder ($\sim$5-μ particles).   In the standard test, 0.25 g of powder was dispersed in 15 ml of solvent.   (This is approximately 1% based on volumes.)   The mixture contained in a 25-ml Erlenmeyer flask was heated at a rate of 5°–10°C/min until the mixture became homogeneous or the solvent boiled.   While heating, the mixtures were agitated vigorously with a Teflon-coated stirring bar.   Temperatures were recorded by an iron/Constantan thermocouple immersed directly in the liquid.

Endpoints were detected by visual observation of the disappearance of turbidity.   They could be reproduced to within ±2°C in most cases. Endpoints in very good solvents ($T_M < 60°C$) tended to be erratic unless polymer and solvent were mixed at temperatures below 10°C.   In other cases mixtures were prepared at room temperature.

The solvents were obtained from a variety of sources and were used as received.   They were practical grade or better.

Annealing and Recrystallization Studies

A high molecular weight sample of PVDC was prepared by mass polymerization at 0°C using azobis(isobutyronitrile) and ultraviolet light as initiator.   Conversion was 10.2%.

Polymer samples were heated in tubes under nitrogen.   The HCl liberated was swept out by N_2 stream and trapped in water.   The amount liberated was determined by titration with standard NaOH solution.   The annealed samples that did not degrade were tested in the standard solution temperature experiment.   The melting points of degraded samples were measured by DTA.

Emulsion polymers were used in recrystallization experiments.   Homogeneous solutions were formed by heating 1% mixtures.   The hot solutions in glass-stoppered Erlenmeyer flasks were transferred to a constant temperature bath at the desired temperature to crystallize.   After crystallization, the samples were transferred isothermally to the hot plate and solution temperatures were measured in the usual manner.

Characterization of Polymer Samples

The melting points of the polymers were measured in a du Pont 900 DTA. The ground powders were packed in 4-mm tubes and heated under nitrogen at 30°C/min. There was evidence that even at this rate the polymers were annealing during the measurement. The T_M values reported here refer to the major peak.

Intrinsic viscosities were measured in tetramethylene sulfoxide (Aldrich). The solvent was analyzed by potentiometric titration. It contained 3.2% tetramethylene sulfone and a trace of H_2O.

Viscosities were measured in a Cannon-Ubbelhode dilution viscometer. Three independent determinations were made for each sample. Flow times were greater than 100 sec in all cases.

RESULTS

Solution temperatures of the various polymers in tetramethylene sulfide (TMS) were measured both "as polymerized" and after recrystallization at 64°C. These results together with other characterization data are shown in Table I. The data indicate that solution temperatures are not signifi-

TABLE I
Properties of Polymer Samples

Sample	$[\eta]$, dl/g	$T^0{}_M$, °C	$T_M(A)$,[c] °C	$T_M(R)$,[d] °C
Emulsion No. 1	—	200	87	—
2	0.343[a]	202	88	93
3	0.440[b]	201	86	94
4	0.700[a]	200	89	92
5	0.577[a]	200	88	93
6	0.930[a]	199	89	93
Mass No. 1	1.61[d]	200	—	—

[a] In TMSO at 25°C.
[b] In TMSO at 60°C.
[c] $T_M(A)$, 1% solution temperature in TMS, as polymerized.
[d] $T_M(R)$, 1% solution temperature after recrystallization at 64°C.

cantly affected by molecular weight over the range covered. Solution temperatures in a wide variety of solvents were measured by the standard method. Values of T_M ranging from 28°C to 180°C were observed.

For purposes of this study, nonsolvents have been defined as those cases in which either the solvent boiled before the polymer dissolved or where the mixture melted into two liquid phases. For practical purposes, however, solvents which do not dissolve PVDC below ~140°C are of little value. The polymer decomposes even in the solid state at these temperatures. Data obtained in annealing experiments show this very clearly; HCl is eliminated and the melting point of the polymer falls with exposure time (Table II). In cases where the solvent was a fairly strong base, such as

TABLE II
Effect of Annealing at 160°C on Melting Point of PVDC

Exposure time, hr	Decomposition,[a] %	T_M, °C
0	0.0	200
1.25	0.92	197
2.25	1.40	196
4	2.72	192
12	11.9	167
24	21.4	[b]
48	37.4	—

[a] g HCl released/g HCl available × 100.
[b] No observable melting point.

pyridine, the polymer decomposed even at low temperatures.   These compounds are not categorized as solvents even though they dissolve the polymer.

The solvents can be grouped in three general classes: nonpolar (Table III), polar aprotic (Table IV), and hydrogen bonding (Table V).   In addition, there are several types of solvents which show an unusual affinity for PVDC.   These cases are tabulated separately.   They include cyclic sulfides (Table VI), cyclic ketones (Table VII), sulfoxides (Table VIII), dialkylamides (Table IX), and substituted lactams (Table X).

The relative ability of the various solvents to dissolve PVDC can be judged by comparing 1%-solution temperatures.   This concentration gave fairly accurate endpoints.   Lower concentrations down to 0.1% were also

TABLE III
Nonpolar Solvents for Poly(vinylidene Chloride)

Solvents	V_1, cc/mole	δ_1	T_M, °C
Bromoform	88.0	10.5	124
1,2-Dibromoethane	86.6	10.4	125
1,3-Dibromopropane	102.4	10.1	126
Bromobenzene	105.5	10.0	129
α-Chloronaphthalene	136	10.4	134
2-Methylnaphthalene	140	9.8	134
1,2-Dibromopropane	105	9.6	134
o-Dichlorobenzene	94.9	10.2	135
Cyclohexyl bromide	123	9.1	136
p-Bromotoluene	124	9.9	138
1,5-Dibromopentane	—	—	140
Tetrahydronaphthalene	137	9.5	142
1,2,4-Trichlorobenzene	125.3	9.9	146
Arochlor 1248	—	8.8	152
Diphenylmethane	168	9.6	159
Vinyltoluene	—	9.1	163
o-Ethyltoluene	137	8.9	164
Decahydronaphthalene	154	8.3	169
Dicyclohexyl	—	—	176

TABLE IV
Nonspecific Polar Aprotic Solvents for PVDC

Solvent	V_1, cc/mole	δ_1	T_M, °C
Nitrobenzene	102	10.0	127
Benzaldehyde	103	9.4	133
Benzonitrile	103	11.2	136
o-Chloronitrobenzene	—	—	140
Di-n-butyl-N,N-diethylphosphoramide	—	—	143
Benzyl benzoate	189	10.1	145
Anisole		10.0	149
γ-Butyrolactone	—	12.6	152
3-Methyltetramethylene sulfone	—	12.9	153
Di-n-butyl sulfone	—	—	155
N,N-Dimethyl-p-toluenesulfonamide	—	—	156
Propiolactone	—	13.4	160
Tetramethylene sulfone	—	—	160
Ethylene diacetate	—	10.0	175
Dimethyl phthalate	163	10.7	176

TABLE V
Hydrogen-Bonding Solvents

Solvent	V_1, cc/mole	δ_1	T_M, °C
Cyclohexanol	106.0	11.4	155
Benzyl alcohol	103.4	12.1	162

TABLE VI
Cyclic Sulfides and Related Solvents

Solvents	V_1, cc/mole	δ_1	T_M, °C
Trimethylene sulfide	74.5	—	74
Tetramethylene sulfide	85.0	9.0	87
1,4-Thioxane	—	—	99
Pentamethylene sulfide	104.2	9.6	106
γ-Thiobutyrolactone	—	—	110
Thioanisole	—	—	130

satisfactory but at high polymer levels, mixing was impaired by the high viscosities of the solutions making endpoints somewhat more difficult to define. A concentration of 1% also falls in the center of the range in which dilute solution studies are usually carried out. As was pointed out in the experimental section, endpoints of 1% mixtures were quite reproducible in most solvents. This was not the case in both very poor solvents and very strong solvents. In the former, where annealing and polymer decomposition or melting into two liquid phases are encountered, endpoints are less reliable.

In very good solvents, wide variations in endpoints were sometimes observed unless samples were mixed cold and heated immediately. This

TABLE VII
Ketone Solvents

Solvent	V_1, cc/mole	δ_1	T_M, °C
Cyclopentanone	89	10.4	106
Cyclohexanone	104	9.9	102
2-Methylcyclohexanone	121	—	115
3-Methylcyclohexanone	122	9.3	116
Cycloheptanone	118	—	96
2,6-Dimethylcyclohexanone	136	—	132
Cyclooctanone	133	—	90
Cyclododecanone	(185)[a]	—	119
Acetophenone	117	10.4	127

[a] Estimated value.

TABLE VIII
Sulfoxide Solvents

Solvent	V_1, cc/mole	δ_1	T_M, °C
Tetramethylene sulfoxide	87.5	12[a]	28
Diisopropyl sulfoxide	—	—	79
Di-n-butyl sulfoxide	—	—	98
Di-n-propyl sulfoxide	—	—	118
Di-p-tolyl sulfoxide	—	—	123
Dimethyl sulfoxide	71.0	13.4	128

[a] Calculated value.

TABLE IX
Dialkyl Amides and Related Compounds

Solvent	V_1, cc/mole	δ_1	T_M, °C
Hexamethylphosphoramide	143	10.5	−7.2[a]
N-acetylpiperidine	114	11.2	35
N-formylhexamethyleneimine	130	—	44
N-formylpiperidine	90.5	11.5	80
N-acetylpyrrolidine	—	11.5	86
N,N-dimethylacetamide	88	10.8	87
N,N-diethylacetamide	124	9.9	104
N,N-dimethylbutyramide	—	—	107
N,N-diethylformamide	112	10.6	111
N,N-dibutylformamide	—	—	113
N-acetylmorpholine	—	11.6	115
N,N,N′,N′-tetramethylthiourea	—	—	121
N,N-dimethylformamide	77.4	12.1	122
N,N,N′N′-tetramethylurea	120	9.6	126
N,N-diallylformamide	—	—	136

[a] M_p of solvent.

seems to be due to the combined effect of aggregation of the polymer particles into gel particles which dissolved more slowly and recrystallization of the swollen gel.

TABLE X
Substituted Lactams

Solvents	T_M, °C
N-methylpyrrolidone	42
N-n-butylpyrrolidone	75
N-vinylpyrrolidone	104
N-benzylpyrrolidone	108
N-acetylcaprolactam	115
N-acetylpyrrolidone	125

The problem of annealing and recrystallization at temperatures slightly below the solution temperature probably exists in other solvents, too. However, by keeping the heating rate fairly low, any rapid changes in crystallinity will occur equally well in all cases. Therefore, the relative order of solvent power based on T_M values will be unchanged. The observed solution temperature depends both on χ_1 and on molar volume. A solvent with small V_1 may be an effective solvent in spite of unfavorable polymer–solvent interaction. Therefore, a direct comparison of T_M values is not indicative of the affinity of solvents for the polymer unless made at constant V_1.

This concept is clearly illustrated by a $1/T_M$ versus $1/V_1$ plot. If the interaction parameter can be written in the form

$$\chi_1 = \chi_s + \frac{BV_1}{RT_M} \tag{2}$$

then eq. (1) can be rearranged to

$$\frac{1}{T_M} = \frac{1}{T_M{}^0 \left[1 + (BV_u v_1{}^2)/(\Delta H_u)\right]} + \frac{(RV_u)/(\Delta H_u)(v_1 - \chi_s v^2)}{\left[1 + (BV_u v_1{}^2)/(\Delta H_u)\right]} \left(\frac{1}{V_1}\right). \tag{3}$$

In an ideal solution where both χ_s and B are zero, the relationship is linear:

$$\frac{1}{T_M} = \frac{1}{T_M{}^0} + \frac{RV_u v_1}{\Delta H_u} \left(\frac{1}{V_1}\right). \tag{4}$$

If polymer–solvent interactions are favorable, $B < 0$; solvents of this type will give solution temperatures falling above the ideal curve described by eq. (4). Solvents forming regular solutions where $B = (\delta_1 - \delta_2)^2$ or solvents forming unfavorable polar mixtures will give solution temperatures falling below this curve.

The best solvents selected from each of the classes are compared in this fashion (Fig. 1).

Four of the five specific solvents fall above the ideal solution range, indicating that $\chi_1 < 0$. The real difference in solvating power can be best appreciated by comparing solution temperatures in two solvents of equal V_1. The difference in T_M between bromoform ($V_1 = 88.0$), the best non-
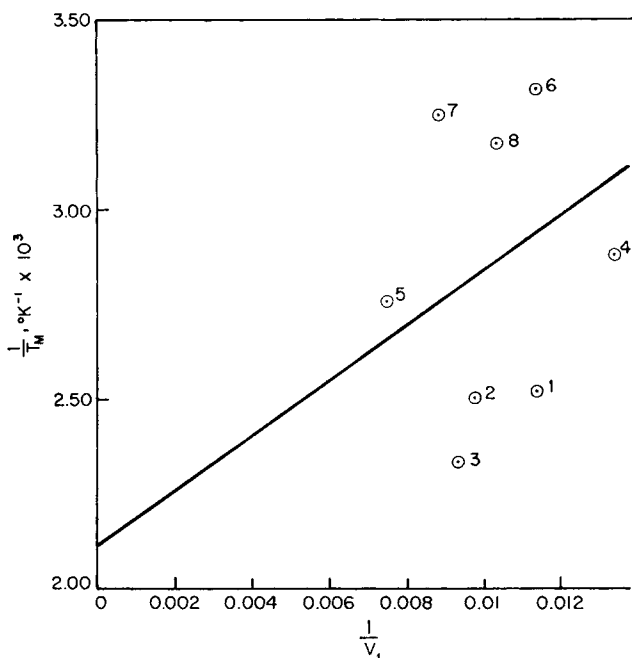
Fig. 1. Comparison of the best solvents in each classification. Solid line-calculated curve for ideal solution behavior: (1) Bromoform; (2) nitrobenzene; (3) cyclohexanol; (4) trimethylene sulfide; (5) cyclooctanone; (6) tetramethylene sulfoxide; (7) N-acetylpiperidine; (6) N-methylpyrrolidone.

polar solvent, and tetramethylene sulfoxide ($V_1 = 87.5$) is 96°C. The plot suggests that χ_1 is positive in bromoform but must be much less than zero in TMSO.

In principle, the interaction parameter for a solvent/polymer pair can be calculated from T_M data. However, eq. (1) applies only to an equilibrium experiment. The measured solution temperatures of crystalline polymers are very sensitive to crystallizaton history, suggesting that these systems are not in true thermodynamic equilibrium.[18-24]

The data collected in this study characterize the solubility of "as polymerized" poly(vinylidene chloride). On comparing the properties listed in Table I, it is questionable whether the polymer is anywhere near being in its most crystalline state. If not, then recrystallizaton or annealing should raise solution temperatures.

As pointed out earlier, annealing of PVDC is complicated by degradation. The emulsion-polymerized polymer starts eliminating HCl above ~130°C.[25] Annealing of emulsion-polymerized PVDC below this temperature does not appear to affect T_M. Above 130°C, annealing can actually reduce the crystallinity of the polymer due to degradation. Annealing for brief periods between 130°–160°C does increase T_M however. Apparently, the amount of degradation occurring under these conditions is not significant.
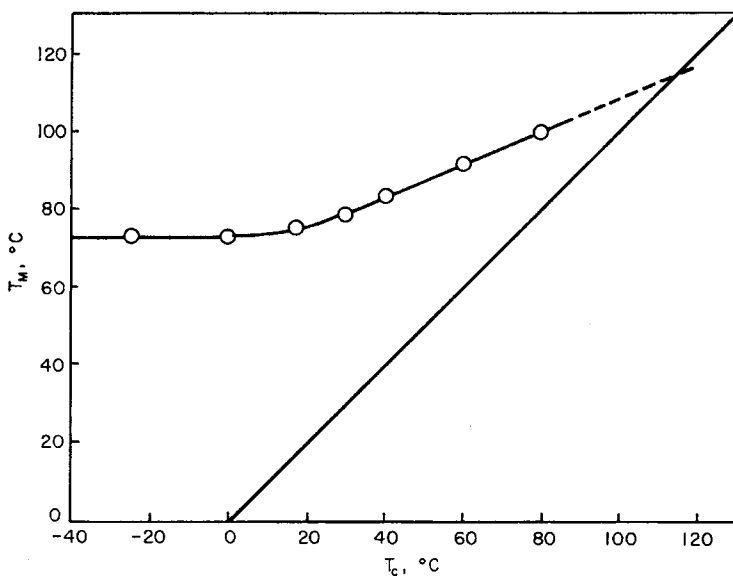
Fig. 2. Effect of crystallization temperature on solution temperature for PVDC in tetramethylene sulfide (0.25 g/15 ml).

For example, annealing for 15 min at 148°C raised the solution temperature in tetramethylene sulfide 5°C above the value for the "as polymerized" polymer.

Recrystallization from solvents can be studied with less danger of degradation. PVDC crystallizes from tetramethylene sulfide over a convenient range, so this system was chosen for study. A plot of T_M versus crystallization temperature of 1% solutions is shown in Figure 2. The extrapolation above the break in the curve should give the equilibrium melting point of pure crystalline PVDC in TMS. This value, 115°C, is significantly higher than either the "as polymerized" sample or the annealed sample. The slope of this line, 0.42, is similar to that observed with other polymers.

The extrapolated T_M would be a better parameter for characterizing solvents since it should be independent on polymer history. However, the same relative scale will still hold; a good solvent for emulsion-polymerized PVDC will also be a good solvent for other samples. Values of B or χ_1 derived from the measured T_M values will be smaller than those obtained from the extrapolated T_M. Therefore, these data should not be used to calculate absolute values of the interaction parameter.

As an illustration, values of χ_1 are calculated for PVDC in TMS using the "as polymerized" value and the "equilibrium" value obtained by extrapolation. These values are -0.02 and $+0.29$, respectively. One might conclude that TMS and PVDC form an ideal solution whereas the "equilibrium" value suggests that the efficiency of TMS in depressing the melt-

ing point of PVDC is due more to a small molar volume than to favorable interaction.

COMPARISON OF SOLVENT CLASSES

Nonpolar Solvents

The best solvents in this class dissolve PVDC only at temperatures where degradation can be a problem.   Assuming solution discoloration is an indicator, PVDC does not decompose significantly in these solvents during short exposures up to 160°C.

Solution temperature data plotted in Figure 3 show that the best solvents in this class have solubility parameters in the range 10.1 ± 0.3. When differences in molar volume are taken into account, α-chloronaphthalene and 2-methylnaphthalene seem to interact most favorably with the polymer.   Mixtures of polymer in solvents with $\delta_1 < 8$ melt into two liquid phases above $\sim$175°C.   The wide variation in solution temperatures in solvents of matching δ_1 cannot be completely accounted for by molar volume differences.   This implies that the solutions are not strictly regular.   The empirical factor χ_s is not zero and apparently varies with solvent structure. To the extent that the solubility parameter scheme can be applied to these solutions, it appears that PVDC has a value of $\delta = 10.1 \pm 0.3$.   The calculated values fall in the same range.
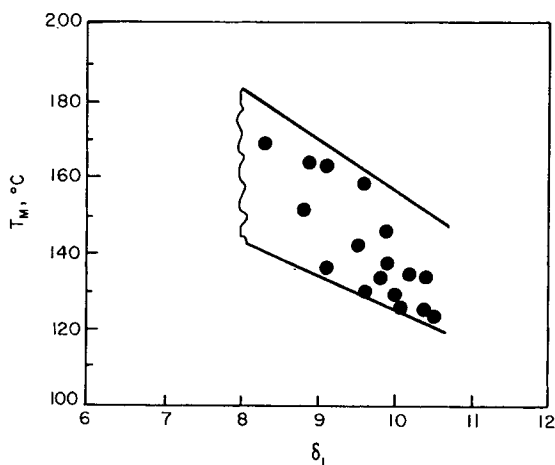

Fig. 3. Correlation between solution temperature in nonpolar solvents and solubility parameter; (0.25 g PVDC/15 ml solvent).

Nonspecific Polar Aprotic Solvents

Solution temperatures in these solvents fall in the same range (130°–180°C) as was found in nonpolar solvents.   There also seems to be a similar correlation with solubility parameter and molar volume.   The two

best solvents, nitrobenzene and benzaldehyde, have low molar volumes and δ_1 close to that estimated for PVDC.

The stability of PVDC in these solvents is considerably less than in non-polar solvents. A significant discoloration was often observed even during the short interval of the solution temperature experiment. Consequently, these solvents are of limited interest. Nitrobenzene is a possible exception. Solutions formed in this solvent appeared to be stable although this could be due only to the lower temperature required to dissolve the polymer.

Hydrogen-Bonding Solvents

Only two solvents were found in this category. Again they both have cyclic structures and low molar volumes. Other alcohols, carboxylic acids, glycols, amides, and the like were not effective in dissolving PVDC. This was true even in cases where δ_1 was low, such as n-octyl alcohol ($\delta_1 = 10.4$). The polymer melted in this solvent to form two liquid phases at 165°C.

Cyclic Sulfides and Related Compounds

The best solvents in this class are, again, ring compounds with low molar volumes. Sulfides are the least polar of the specific solvents (δ_1 values where known, are low). They are relatively water insoluble compared to sulfoxides or the analogous ethers. This is in agreement with their lower dipole moments and reduced proton-binding power.

In all cases where comparisons can be made, the substitution of sulfur for oxygen improves solvent power. This suggests that PVDC interacts more
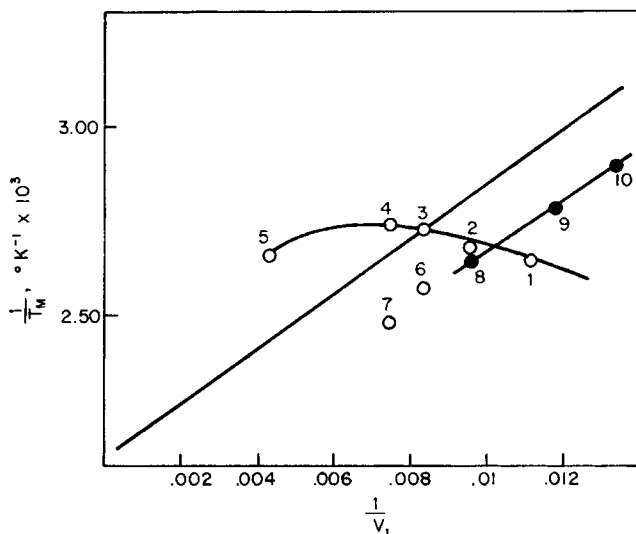

Fig. 4. Effect of ring size on solvent power of cyclic ketones and cyclic sulfides: (1) cyclopentanone; (2) cyclohexanone; (3) cycloheptanone; (4) cyclooctanone; (5) cyclododecanone; (6) 2-methylcyclohexanone; (7) 2,6-dimethyl cyclohexanone; (8) pentamethylene sulfide; (9) tetramethylene sulfide; (10) trimethylene sulfide.

favorably with "soft" bases.[26]   The interaction, however, does not produce negative χ_1 values.   The plot in Figure 4 suggests that these are nearly ideal solutions.   In addition, there appears to be little effect of structure on the nature of the interaction.   The decrease in solvent power with increasing ring size can be attributed mostly to the increase in molar volume.

Cyclic Ketones

The ketones form another interesting group of solvents.   As the list in Table VII implies, none of the aliphatic ketones tested would dissolve PVDC.   In the cyclic ketone series, solvent effectiveness appears to increase with ring size up to eight carbons.   The comparison of these solvents in Figure 4 points up a significant difference between sulfides and ketones. In the latter, an increase in ring size improves polymer–solvent interactions so that solvent power increases in spite of the increase in molar volume. Solution temperatures in substituted cyclohexanones are significantly higher than either the parent compound or larger ring compounds of equivalent molecular weight.   Both the effect of ring size and substitution suggest that nonideal entropy changes are influencing polymer–solvent interaction in these cases.

Sulfoxides

The sulfoxides seem in general to be better solvents than either the sulfides or sulfones.   Unfortunately, not enough examples were available to establish trends.   The cyclic compound, TMSO, was the best of this group, pointing out again that ring structures are desirable.   A comparison between n-propyl and isopropyl sulfoxide suggests that chain branching improves solvent power also.   The solubility parameters of these solvents, where known, are much higher than the value assigned to PVDC.

Dialkyl Amides

A larger number of amides were available for testing.   The ring compounds also lead this classification.   In the two cases where comparisons can be made, an increase in ring size improves solvent power.   (Compare N-formylpiperidene to N-formylhexamethyleneimine.)

What seems to be a reasonable trend can be observed in the dialkyl amides.   As the size of the alkyl groups (or the fatty acid chain) is increased, solution temperatures fall to a minimum and then rise.   This seems to be due to a balance between polarity and molar volume.   The better dialkyl amide solvents have fairly low δ_1 values (between 10 and 11), suggesting that their behavior is at least crudely correlated with solubility parameters.   The ring compounds, on the other hand, have δ_1 values above 11.   All of the amide solvents have high dipole moments and are effective proton acceptors.

HMPA has been included with the amide solvents but it should be viewed as a unique case.   It is the only solvent capable of forming concentrated thermodynamically stable solutions with PVDC at room temperature,

This solvent combines the properties of high base strength and low dielectric constant. Its solubility parameter is low (10.5) but it has a relatively large molar volume. Unfortunately, PVDC does not appear to be stable for very long periods in the presence of HMPA even at room temperature.

Substituted Lactams

These solvents closely resemble the dialkylamides in their properties. However, data on individual numbers other than N-methylpyrrolidone are scarce. Its solubility parameter and molar volume are 11.3 and 96.5, respectively. The values for the other good solvents (excluding HMPA) are similar, suggesting again that polar aprotic solvents with low molar volume and relatively low δ_1 values are the most effective solvents for PVDC.

DISCUSSION

This study shows that PVDC is not unusually insoluble. Like most polar crystalline polymers, it can be dissolved in many solvents at temperatures not too far below its melting point. The lower limit seems in this case to be $\sim 130°C$. Below this temperature, PVDC dissolves only in certain types of solvents: cyclic sulfides, cyclic ketones, sulfoxides, dialkylamides, and alkyl lactams.

The above-named solvents are members of the general class of polar aprotic solvents.[28] These solvents are characterized by high dielectric constants, high dipole moments, and relatively high boiling points. They act as Lewis bases and are powerful hydrogen-bond acceptors but poor proton donors.

Within this group of solvents, however, affinity for PVDC varies significantly. Solvents such as sulfones, lactones, nitriles, esters, sulfonamides, and phosphate esters, among others, show no unusual ability to dissolve PVDC. Their behavior is not very different, in fact, from that of nonpolar solvents.

The polar character of PVDC does not seem to be important except in specific solvents. In these solutions, however, PVDC must be acting as weak Lewis acid. Interaction parameters estimated from the solution temperature measurements are negative in some cases as would be expected in an acid–base mixture.

The most likely site for interaction in the PVDC chain is the methylene hydrogen. Normally, one does not think of aliphatic hydrogen as being acidic. But if electron-withdrawing groups such as halogen are substituted on the same or adjacent carbon atoms, acidity is significantly enhanced.[29] This suggests that the dichloromethylene units in the PVDC chain are producing this effect in PVDC.

An interaction of this type would explain why PVDC is solubilized only by dipolar aprotic solvents that are good H-bond acceptors. Many of the good solvents found in this study are found to bond strongly both to

phenol[30] and chlorinated hydrocarbons.[27,29] The best solvent, HMPA, actually forms complexes with the latter.[30] The specificity of solvent structure implies that the entropy of interaction must also be important in the case of PVDC.

References

1. R. C. Reinhardt, *Ind. Eng. Chem.*, **35**, 422 (1943).

2. K. Okuda, *J. Polym. Sci.*, **2**, 1749 (1964).

3. H. Burrell, *Official Digest*, 1955, p. 726.

4. H. Burrell and B. Immergut, *Polymer Handbook*, Interscience, New York, 1966, p. IV–360.

5. P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).

6. W. Goggin and R. Lowry, *Ind. Eng. Chem.*, **34**, 327 (1942).

7. R. W. Eykamp, A. M. Schneider, and E. W. Merrill, *J. Polym. Sci. A*, **4**, 1025 (1966).

8. J. H. Hildebrand and R. L. Scott, *Regular Solutions*, Prentice Hall, New York, 1963.

9. H. Morawetz, *Macromolecules in Solution*, Wiley, New York, 1965.

10. P. J. Flory, *Principles of Polymer Chemistry*, Cornell U. Press, Ithaca, N. Y., 1953, Chap. XIII.

11. R. L. Adelman and I. M. Klein, *J. Polym. Sci.*, **31**, 77 (1958).

12. *Polymer Handbook*, p. IV–195.

13. H. W. Coover, Jr., and J. B. Dickey, U. S. Pat. 2,742,444 (1956).

14. R. C. Houtz, U.S. Pat. 2,460,578 (1949).

15. R. C. Houtz, U.S. Pat. 2,460,579 (1949).

16. D. A. Baggett and H. H. McClure, U.S. Pat. 2,886,547 (1959).

17. D. M. Woodford, *Chem. Ind.*, 1966, p. 316.

18. J. B. Jackson, P. J. Flory, and R. Chiang, *Trans. Faraday Soc.*, **59**, 1906 (1963).

19. V. F. Holland, *J. Appl. Phys.*, **35**, 59 (1964).

20. R. Chiang, J. H. Rhodes, and V. F. Holland, *J. Polym. Sci. A-2*, 479 (1965).

21. R. Chiang, *J. Polym. Sci.*, **3**, 2019 (1965).

22. J. F. Kenny and V. F. Holland, *J. Polym. Sci. A-1*, **4**, 699 (1966).

23. J. F. Jackson, L. Mandelkern, and O. C. Long, *Macromolecules*, **1**, 218 (1968).

24. J. F. Jackson and L. Mandelkern, *Macromolecules*, **1**, 546 (1968).

25. R. D. Böhme and R. A. Wessling, to be published.

26. R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

27. H. Normant, *Angew. Chem. (Int. Eng. Ed.)*, **6**, 1046 (1968).

28. A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

29. E. Halpern, J. Houck, H. Finegold, and J. Goldenson, *J. Amer. Chem. Soc.*, **77**, 4472 (1955).

30. D. P. Eyman and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 1617 (1966).