Solubility Properties of Poly(1,1-Difluoroethylene) in Dipolar Aprotic Solvents

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Synopsis

A screening study of the solubility of poly(1,1-difluoroethylene) (PVF$_2$, $\overline{M}_w = 2 \times 10^5$) at room temperature in a wide variety of dipolar aprotic species has facilitated the discovery of a series of new solvents (*N*-methyloxazolidone, cyclic-substituted ureas) and rationalization of the data in a two-dimensional solubility map involving their dipole moment, μ, and their hydrogen-bond-accepting (HBA) power β (Taft solvatochromic parameter). This map may be used as a predictive tool for the research of new functional classes of solvents, such as *N*-substituted mixed amide-ester of phosphoric acid or *N*-substituted sulfurous diamides. The variations of the intrinsic viscosity of the polymer with solvent polarity may be quantitatively analyzed using a linear multiparametric correlation which emphasizes the two opposite contributions of cavitation effects (Hildebrand solubility parameter δ) and of polymer–solvent interactions (β) on the coil expansion: $[\eta]$ (dL.g^{-1}) $= 0.792 - 1.2 \times 10^{-3}\delta^2$(J.cm^{-3}) $+ 1.59 \beta$. Finally, 1,3-dimethyl-2-oxo-hexahydropyrimidine (*N,N'*-dimethylpropylene urea) leads to the highest value of the refractive index increment ($dn/dc = -0.065$ mL.g^{-1} at $\lambda = 632$ nm), and thus appears as the best solvent for light-scattering measurements.

INTRODUCTION

Because of its excellent chemical resistance and ferroelectric properties poly(1,1-difluoroethylene) (PVF$_2$) may be considered as a representative specialty polymer of rapidly growing importance in various fields such as coatings, chemical processing equipment, and piezo- and pyroelectric applications.[1,2] Its crystallinity and polarity strongly restrict its solubility to dipolar aprotic solvents,[1-3] and the research for new solvents, especially good solvents at room temperature, is still of interest for better molecular characterization through dilute solution measurements (light scattering) as well as for extended possibilities of PVF$_2$ processing through solution casting.

The purpose of this communication is to present a screening study of PVF$_2$ solubility in a wide variety of solvents with two main goals: First, the search of new functional classes of solvents, and the rationalization of the PVF$_2$ solubility properties within the framework of a solubility map emphasizing the major contributions of specific dipolar and hydrogen-bonding interactions to PVF$_2$ solubility. Second, the semiquantitative analysis of the chain expansion in dilute solution, as measured by the intrinsic viscosity values, in terms of solvent cavitation effects and of specific polymer–solvent interactions.

EXPERIMENTAL

Solvents and Polymers

All the solvents of the best reagent grade were used after drying on freshly regenerated molecular seives 4 Å. Experimental laboratory PVF_2 samples were obtained from ATOCHEM, purified by precipitation of their dimethylformamide solutions into a large excess of water, further thoroughly washed with methanol in a Waring blender, and finally dried at 60°C under 10^{-2} torr.

Solubility Tests

These tests were performed at a concentration of 1 g.dL^{-1} on finely ground samples. When solubilization was not achieved within 1 h at a temperature lower than 50°C, the following procedure was followed: samples were heated for 2 h at 85°C under gentle stirring, slow cooling, and annealing for 2 h at room temperature.

Viscometric Measurements

They were carried out on an automatic Fica device at 25°C for a concentration range of 0.1 to 0.8 g.dL^{-1}. Solubilization of the polymer was achieved most often at a temperature lower than 50°C, except in the case of poor solvents (γ-butyrolactone) where the previous thermal treatment was adopted. The intrinsic viscosity $[\eta]$ (dL.g^{-1}) and the Huggins constant K'_H were calculated according to Sakai's procedure[4] (most reliable K'_H values).

Light-Scattering Experiments

The values of the refractive index increments dn/dc (mL.g^{-1}) were measured on a Brice-Phoenix differential refractometer at room temperature, for $\lambda = 546$ and 632 nm. Light-scattering experiments were performed at room temperature on an Amtec SM-200 apparatus.

RESULTS AND DISCUSSION

The known solubility properties of PVF_2[1-3] and a recent analysis of the thermodynamics of interaction between PVF_2 in the liquid state (160 < t°C < 200) and a wide variety of solutes[5] clearly suggest that potential solvents should belong to the dipolar aprotic ones showing high enough dipole moments and hydrogen-bond-accepting (HBA) strengths. Specific polymer–solvent interactions arise from dipole interactions involving the highly dipolar C—F bond and also, very likely, from hydrogen bonding involving the "acidic" methylene carbon of the chain[5] (electro-withdrawing effects of the two neighboring CF_2 groups). Thus, instead of relying on the popular solubility parameter concept,[6] the selection of the potential solvents was performed according to their dipole moment μ and their HBA strength as measured by the empirical solvatochromic parameter β introduced by Kamlet et al.[7,8] Among the many solvent basicity scales, the reliability of the β parameter, as a good descriptor of Gibbs energy of hydrogen bonding between HBA solvents and hydrogen bond-donating solutes, has been reemphasized very recently.[9]

All the $\mu^{10,11}$ and β^8 values were taken from literature compilations or from original publications. In the following text a figure given within parentheses is ascribed to every solvent.

The Solubility Map of PVF$_2$

The results of the solubility tests performed on a PVF$_2$ sample of $\overline{M}_w = 2.01 \times 10^5$ may be discussed according to the functional group of the solvents.

Aliphatic and aromatic ketones. Cyclohexanone (1), acetophenone (2), and benzophenone (3) are well known solvents at high temperatures;[1-3] in our hands, cyclopentanone (4) leads to stable solution even at room temperature (RT).

Esters, lactones and carbonates. Among the more polar carboxylic esters and related compounds, only γ-butyrolactone $O(CH_2)_3\!-\!CO$ (5) and pro-pylenecarbonate[12] $O\!-\!CH(CH_3)\!-\!CH_2\!-\!O\!-\!CO$ (6) ($\mu = 4.94$ D, $\beta = 0.40$) yield solutions which tend to gel on annealing at RT, more rapidly in the latter case. Trimethyl- and triethylphosphates (7 and 8), dimethyl methylphosphonate (9) ($\mu = 2.88$, $\beta \sim 0.82$) are good solvents whereas tri-n-butylphosphate (10) ($\mu = 3.1$ D, $\beta \sim 0.63$) is only a swelling agent. Trimethylphosphite (11) ($\mu = 1.81$ D, β unknown) on the other hand is a nonsolvent: this feature emphasizes the prominent contribution of the $P\!=\!O$ double bond to the polarity of these species.[13]

Tertiary amides. Open-chain or cyclic carboxylic amides such as dimethyl- and diethylformamide (12, 13), dimethylacetamide (14), N-formylmorpholine $H\!-\!CO\!-\!N(CH_2)_2\!-\!O\!-\!(CH_2)_2$ (15) and N-methylpyrrolidone (16) are well known quality solvents for PVF$_2$. Hexamethylphosphoric triamide (17) probably may be considered the best one (see further), and the closely related methyltetramethylphosphorodiamide[14] $CH_3\!-\!P(O)\!-\![N(CH_3)2]_2$ (18) ($\mu = 4.8$ D, β unknown) is also a very good solvent. Finally, N,N,N',N'-tetraethylsulfamide[15] $(H_5C_2)_2\!-\!N\!-\!SO_2\!-\!N\!-\!(C_2H_5)_2$ ($\mu = 2.8$ D, $\beta = 0.52$) is a nonsolvent.

2 - A l k y l o x a z o l i d o n e s . 3 - M e t h y l - 2 - o x a z o l i d o n e[16] $O\!-\!CH_2)_2\!-\!N(CH_3)\!-\!CO$ (20) (μ and β unknown), representative of N-alkylcyclic urethanes, is a good solvent of PVF$_2$ at RT.

Ureas. Open-chain[17] and cyclic-substituted ureas[18] such as tetramethylurea (21), 1,3-dimethyl-2-imidazolidinone $(CH_3)N\!-\!(CH_2)_2\!-\!N\!-\!(CH_3)\!-\!CO$ (22) (N,N'-dimethylethyleneurea) and 1,3-dimethyl-2-oxo-hexahydro-pyrimidine $(CH_3)N\!-\!(CH_2)_3\!-\!N(CH_3)\!-\!C'O$ (23) (N,N'-dimethylpropyleneurea) are good solvents for PVF$_2$ at RT.

Sulfoxides and sulfones. The well known solubility of PVF$_2$ in dimethylsulfoxide (24) may be opposed to its insolubility in tetramethylenesulfone (tested in presence of 5% by vol of 3-methyltetramethylenesulfone to avoid crystallization at RT) $(CH_2)_4\!-\!SO_2$ (25) ($\mu = 4.81$ D, $\beta = 0.35$).

Pyridines. In spited of high HBA strengths pyridine (26), and its substituted derivatives such as 3-methyl (27), 4-methyl (28), 2,4-dimethyl (29), and 2,4,6-trimethyl (30) pyridines ($\mu = 2.2 - 2.6$ D, $\beta = 0.67 - 0.74$) are nonsolvents of PVF$_2$.
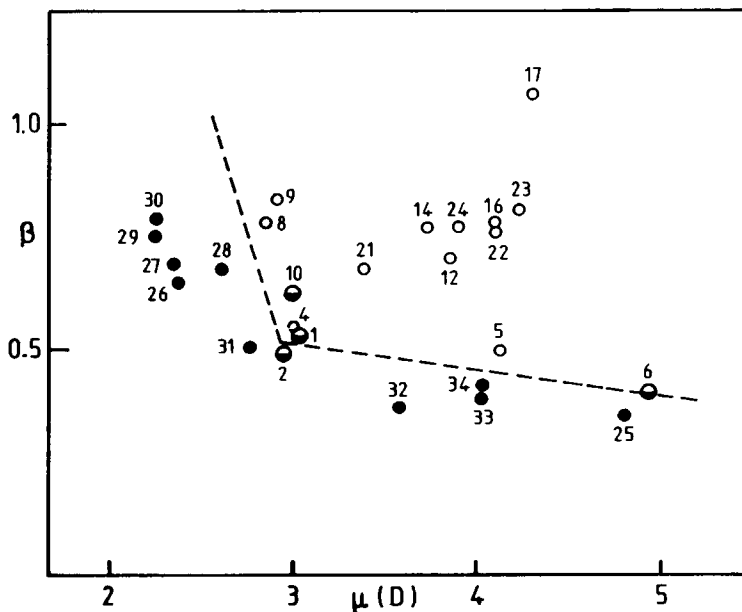
Fig. 1. Solubility map of PVF_2 in dipolar aprotic solvents at RT. O, solvents; ●, nonsolvents; ◐, borderline solvents.

The previous data allow derivation of a semiquantitative solubility map of PVF_2 in dipolar aprotic solvents, using the μ and β polarity parameters as coordinates (Fig. 1). The transition between solubility and insolubility may be roughly defined by the border line solvents leading most often to gel-like solutions at RT (species 1,2,6) and by the non-solvents previously quoted (25-30) together with some other non-solvent species such as 2-pentanone (31), propionitrile (32), nitrobenzene (33), and benzonitrile (34).

In spite of its semi-quantitative character, this map is of interest from two complementary viewpoints:

First, it allows a first insight into the respective contributions of dipolar and hydrogen-bonding interactions in the solvation process of the PVF_2 chain: strong HBA power ($\beta > 0.7$) associated with moderate polarity ($\mu \sim 2.7$ D) appears much more efficient in promoting solubilization than high polarity ($\mu > 4$ D) associated with relatively weak HBA strength ($\beta < 0.4$).

Second, it allows rationalization of the research for new solvents (Table I). For instance, N-substituted mixed amide-esters of phosphoric acid[19] such as compounds (36) and (37) are likely to be good solvents of PVF_2 at RT: neglecting variations in steric orientation of the phosphorous atom substituents, they may be considered as intermediates between hexamethylphosphorotriamide and triethylphosphate (successive substitution of dimethylamino groups by ethoxy ones). Moreover, within the series of nine sulfamides, sulfonamides, sulfurous diamides, and sulfinamides very recently proposed as new dipolar aprotic solvents,[15] one good solvent (38) and three borderline ones or swelling agents (39-41) could probably be found. Finally, the aliphatic or aromatic amine N-oxides of strong zwitterionic character ($\geq N^+ - O^-$ is the major mesomeric form), which show very high dipole

TABLE I
Prediction of PVF$_2$ Solubility at RT in new Dipolar Aprotic Solvents

	Solvents	μ(D)	β	Solvent power
(35)	H_3C—O—⬡—N	3.05	0.72	+
(36)	H_5C_2—O—P—[N(CH$_3$)$_2$]$_2$ ‖ O	3.28	unknown	+
(37)	(H$_3$C)$_2$—N—P—(O—C$_2$H$_5$)$_2$ ‖ O	2.93	0.88	+
(38)	(H$_3$C)$_2$—N—S—N(CH$_3$)$_2$[a] ‖ O	3.1[d]	0.61	+
(39)	—(CH$_2$)$_4$—N—S—N(CH$_2$)$_4$—[b] ‖ O	3.1[d]	0.51	±
(40)	(CH$_3$)$_3$—C—S—N(C$_2$H$_5$)$_2$ ‖ O	2.3[d]	0.74	±
(41)	(CH$_3$)$_3$—C—S—N—C$_2$H$_5$)$_2$ ‖ O	2.7[d]	0.59	±
(42)	⬡—N$^+$— O$^-$ [c]	4.2	0.85	+

[a] $t_m = 31°C$.
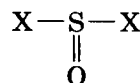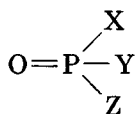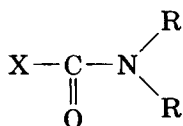[b] $t_m = 25°C$.
[c] $t_m = 64°C$.
[d] Approximate μ values derived from the experimental values of the Taft solvatochromic parameter Π^* Ref. 15, according to: $\mu(D) \sim -0.1 + 4.3\Pi^*$ Ref. 7.

moments[20] ($\mu > 4$ D) and HBA strengths[8] ($\beta > 0.8$), would be very interesting potential solvents: to the best of our knowledge, however, none of these species exists in the liquid state at RT.[20, 21]

To conclude, all the good solvents of PVF$_2$ at RT may be ordered in three main series essentially defined by the presence of the dipolar C=O, P=O, and S =O bonds, as outlined below:

$$X—\underset{\underset{O}{\|}}{C}—N\overset{R}{\underset{R}{\diagup\diagdown}} \qquad O=P\overset{X}{\underset{Z}{\diagup\diagdown}}Y \qquad X—\underset{\underset{O}{\|}}{S}—X$$

X = R, OR or NR$'_2$ X = Y = Z = OR or NR$_2$ X = R or NR$_2$

X = R, Y = Z = OR or NR$_2$

X = Y + OR; Z = NR$_2$

X = Y = NR$_2$; Z = OR

TABLE II
Intrinsic Viscosities $[\eta]$ and Flory Interaction Parameters χ at
Solvent Infinite Dilution for Various PVF_2–Solvent Systems

Solvents	δ^b (J.cm^{-3})$^{0.5}$	μ D^a	β	$[\eta]$ (25°C) dL.g^{-1}	K'_H	χ 25°C	170°C
(17) HMPA	18.9	4.3	1.05	1.85	0.19	− 1.7	− 1.2
(8) TEP	16.8	2.86	0.77	1.70	0.25		
(23) DMPU	23.1	4.23	0.80	1.57	0.25	− 1.5	− 0.81
(22) DMEU	23.0	4.09	0.76	1.56	0.22	− 1.4	− 0.76
(21) TMU	20.7	3.37	0.66	1.45	0.33	− 1.3	− 0.73
(14) DMAC	22.6	3.72	0.76	1.47	0.21	− 1.3	− 0.78
(12) DMF	24.1	3.86	0.69	1.32	0.28	− 1.5	− 0.71
(13) DEF	20.7	3.9	0.70	1.37	0.25		
(16) NMP	23.8	4.09	0.77	1.30	0.43	− 1.5	− 0.75
(20) MOX				1.22	0.26		
(24) DMSO	24.5	3.9	0.76	1.17	0.34	− 1.0	− 0.5
(4) CPONE	21.1	3.0	0.54	1.02	0.49		− 0.1
(5) γBL	25.8	4.12	0.49	0.62		0	− 0.03

^{a} 1 Debye = 10^{-18}esu = 3.336×10^{-30} Coulombmeter.
^{b} $\delta^2 = (\Delta H_v - RT)/V$

Analysis of Polymer-Solvent Interactions

The intrinsic viscosity $[\eta]$ and the Huggins coefficient K'_H were measured at 25°C for the same PVF_2 sample previously used for the solubility tests ($\overline{M}_w = 2.01 \times 10^5$) in a series of solvents representative of all types of functionality: the experimental results are given in Table II. The $[\eta]$ values cover a relatively wide range from about 0.6 (γ-butyrolactone) to about 1.8 dL.g^{-1} (hexamethylphosphorotriamide) and if the data related to γ-butyrolactone are omitted (molecular dispersion is not fully ascertained in this very poor solvent), as a general trend, the K'_H values are a decreasing function of $[\eta]$, in good agreement with the expected decrease of the Huggins constant when increasing chain expansion.[22]

Comparison Between Intrinsic Viscosity (Polymer Infinite Dilution) and Gas-Liquid Chromatographic Data (Solvent Infinite Dilution)

A previous study of the thermodynamics of interactions between PVF_2 in the liquid state (160–200°C) and a series of low-molecular weight probes at infinite dilution[5] was recently extended to most of the new dipolar aprotic solvents used in this work:[23] the values of the Flory interaction parameter χ measured at 170°C or extrapolated to 25°C are given in Table II. $[\eta]$ and χ both reflect polymer–solvent interactions, but their comparison is necessarily biased by the possible concentration dependence of χ, by the high temperature gap between $[\eta]$ and χ measurements or by the low accuracy of the extrapolated χ values (the relation $\chi = A + B/T$ does not necessarily hold over such a broad temperature range). The observed correlations given in Figure 2 are, however, statistically meaningful (see regression coefficients R and mean square standard deviations σ), and the observed trend is well
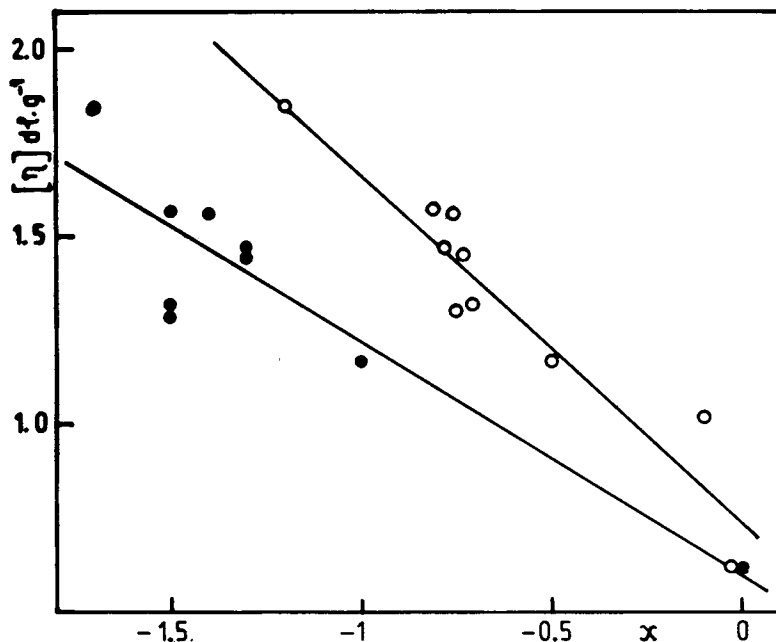
Fig. 2. Correlation between the intrinsic viscosities of a PVF$_2$ sample ($\overline{M}_w$ = 2.01 × 10^5) in solution in various solvents and the Flory χ interaction parameter measured by GLC at infinite dilution of the same solvents. O, χ measured at 175°C; ●, χ extrapolated at 25°C.

ascertained: the order of polymer–solvent interactions is the same in the two extreme concentration ranges of the binary solutions.

$$[\eta]\text{dL.g}^{-1} = 0.740 - 0.930\,\chi_{170};\ \text{R}(10) = -0.949,\ \sigma = 0.11$$

$$[\eta]\text{dL.g}^{-1} = 0.599 - 0.617\,\chi_{25};\ \text{R}(9) = -0.913,\ \sigma = 0.15$$

Chain Expansion in Dilute Solution as a Function of Solvent Polarity

The $[\eta]$ variations cannot be satisfactorily rationalized within the framework of solvent solubility parameters[6] (either the Hildebrand ones (δ) given in Table II or the more sophisticated three-dimensional ones). They may be, however, tentatively correlated with a series of solvent polarity parameters (δ, μ, and β) using linear multiparametric correlation analysis, by analogy with the most successful "Linear Solvation Energy Relationships" introduce by Taft et al. for the interpretation of standard free energies of transfer of solutes from solvents to solvents:[8, 24, 25]

$$[\eta] = [\eta]_0 + d\delta^2 + m\mu + b\beta$$

In this equation (which is obviously molecular weight dependent) the first δ^2 term is a measure of the cavitation energy necessary to disrupt solvent–solvent interactions and to create a suitably sized hole to accommodate the solute chain, while the two following terms are related to solute–solvent interactions. The correlation matrix given below shows that δ^2,
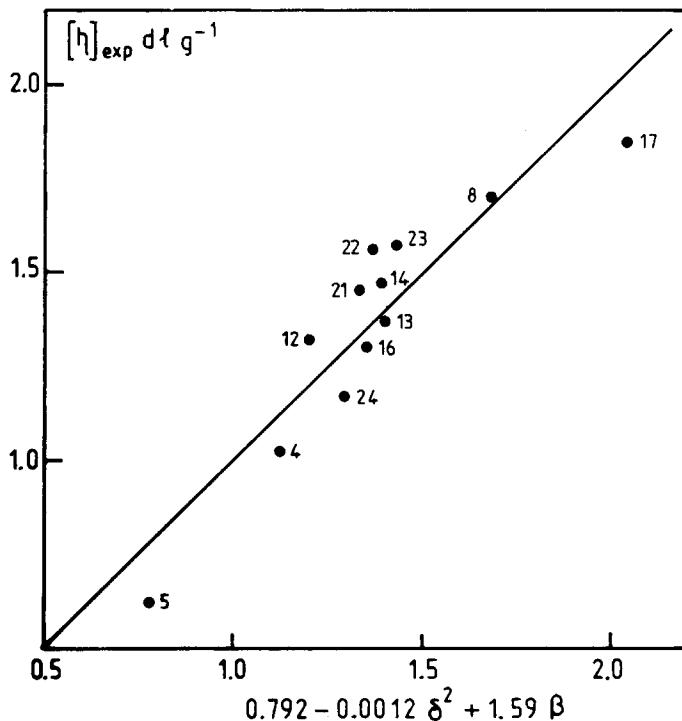
Fig. 3. Experimental versus calculated $[\eta]$ values at 25°C for PVF$_2$ ($\overline{M}_w = 2.01 \times 10^5$) in solution in various dipolar aprotic solvents.

μ, and β are actually independent variables for the solvent set experimentally involved.

	δ^2	μ	β	$[\eta]$
δ^2	1	0.546	-0.422	-0.683
μ		1	0.384	0.015
β			1	0.848

Correlation analysis leads to (see also Fig. 3):

$$[\eta]\mathrm{dL.g}^{-1} = 0.793 - 0.0012\delta^2 + 1.59\beta; \; R(12) = 0.921, \; \sigma = 0.14$$

According to F statistics,[26] the introduction of the μ term does not give any significant improvement of the correlation.

Because of its relatively too-low accuracy, the previous empirical correlation cannot be used as a very reliable predictive tool, but it still remains of interest for a semiquantitative analysis of the $[\eta]$ variations at a molecular level. Cavitation effects correspond to an endothermic process (the coefficient of the δ^2 term is negative) and opposed to the exothermic solute-solvent interactions (the coefficient of the β term is positive). The comparison of these coefficients, recalculated using centered variables to take into account their different variation ranges,[27] shows that hydrogen-bonding interactions are the major factor accounting for about 63% of the observed $[\eta]$ variations in the solvent

population involved: this is very likely for the polar binary solutions investigated where polymer–solvent interactions should prevail over cavitation effects. Finally the intercept, $[\eta]_0 = 0.79$ dL.g^{-1} may be identified with the intrinsic viscosity of the chain dissolved according to a pure athermal process (Hildebrand ideal solution), but it must not be confused with the intrinsic viscosity in a θ medium when enthalpic and excluded volume effects cancel each other.

Chain Expansion in Dilute Solution with Respect to the θ State

The determination of the viscosimetric expansion coefficient α_η requires the knowledge of the unperturbed dimensions K_θ. Unfortunately, the literature data[28-30] are rather confusing leading to K_θ values between 2.7×10^{-4} and 3.4×10^{-3} dL.g^{-1}, depending on temperature and solvent. Moreover, the experimental $[\eta] - \overline{M}_w$ data of our sample are not consistent with the viscosimetric equation given by Welch for DMAC solutions at 25°C:[29] $[\eta]_{\text{exp}} = 1.47$ versus $[\eta]_{\text{calc.}} = 0.75$ dL.g^{-1}. The possible calculation of K_θ from intrinsic viscosities of a single polymer sample in a series of different solvents involves the determination of the "crossover" concentration at which all the linear variations of C/η_{sp} versus C (Heller equation) are expected to converge:[31] this approach completely fails for our measurements. Finally, extrapolation of the experimental $[\eta] - K'_H$ data to the theoretical $K'_{H,\theta}$ values of 0.50[22] or 0.52[32] leads to an upper limit of $[\eta]_\theta$ of about 1 dL.g^{-1} for our sample: according to this very rough approximation, the maximum chain expansion observed in hexamethylphosphoramide would correspond to a lower α_η limit of about 1.23; on the other hand, the PVF$_2$ chain would exist in a collapsed configuration in γ-butyrolactone, characterized by a minimum α_η value of about 0.85.

Light-Scattering Measurements

The values of the refractive index increments dn/dc (mL.g^{-1}) measured at room temperature are given in Table III. Within the Gladstone-Dale approximation,[33] their variations with the refractive index of the solvent n_D

TABLE III
Refractive Index Increments of PVF$_2$ in Solution at RT

Solvent	η_D^{25}	dn/dc mL.g^{-1}	
		$\lambda = 632$ nm	$\lambda = 546$ nm
(23) DMPU	1.4881	-0.065	-0.067
(25) TMS	1.4850	-0.063	-0.064
(24) DMSO	1.4773	-0.060	-0.062
(22) DMEU	1.4707	-0.053	-0.055
(16) NMP	1.4680	-0.050	-0.052
(17) HMPA	1.4570	-0.044	-0.046
(21) TMU	1.4493	-0.040	-0.042
(14) DMAC	1.4356	-0.031	-0.033
(12) DMF	1.4305	-0.021	-0.023

obey the semiempirical relationships:

$$\lambda = 632 \text{ nm}: dn/dc(\text{mL.g}^{-1}) = 0.9115 - 0.6562 \, n_D;$$

$$R(8) = 0.995, \sigma = 0.0013$$

$$\lambda = 536 \text{ nm}: dn/dc(\text{mL.g}^{-1}) = 0.8977 - 0.6481 \, n_D;$$

$$R(8) = 0.994, \sigma = 0.0013$$

The average value of the apparent partial specific volume of PVF_2 in solution, $\bar{v} \sim 0.650$ mL.g^{-1}, is about 9% higher than that calculated for amorphous PVF_2,[34] $v = 0.598$ mL.g^{-1}. This difference, slightly stronger than that generally observed for less polar systems,[33] may arise, at least partly, from the misuse of the n_D values instead of the actual ones at $\lambda = 632$ and 536 nm.

None of the solvents tested displays *simultaneously* high solvation power to avoid possible aggregation phenomena, high dn/dc to afford good sensitivity, and perfect chemical inertness with respect to PVF_2 dehydrofluorination. Dimethylpropyleneurea (DMPU), a good solvent which shows the highest dn/dc value, is basic enough to induce a very slight discoloration of the PVF_2 solution as observed with most of the other good solvents. Light-scattering measurements on a series of laboratory samples of relatively low molecular weights ($1-2.5 \times 10^5$) dissolved in DMPU proved to be straightforward, leading to $\overline{M}_w$ values in fairly good agreement with those determined in DMAC or NMP solution, providing that experiments were performed on freshly prepared solutions and solubilization achieved at a temperature lower than 50°C.[35] Annealing of the DMPU solutions at RT leads to a simultaneous increase of the discoloration and of the second virial coefficient B. The following $\overline{M}_w$ and B data obtained in DMAC, NMP, and DMPU, respectively, are quite representative: $\overline{M}_w \times 10^{-5} = 1.15$, 1.08, and 1.01; B $\times 10^3$ mol/mL.g^{-1} = 1.1, 1.2, and 1.5 (2.00 after 24 h annealing at RT). The differences observed between the three $\overline{M}_w$ values merely reflect the rather poor accuracy of the measurements arising from the low dn/dc values, especially for DMAC and NMP (see Table III) and from possible perturbations due to the slight discoloration of the solutions. The highest B value measured in DMPU is consistent with the highest $[\eta]$ one observed in the same solvent. Finally the solutions obtained at higher solubilization temperature or by long lasting annealing are more strongly colored whatever the solvent is and the significant resulting fluorescence requires suitable correction.[36]

CONCLUSION

A screening study of PVF_2 solubility at room temperature in a wide variety of dipolar aprotic solvents has allowed:

1. The discovery of new functional series of good quality solvents such as oxazolidones or cyclic ureas: dimethylpropyleneurea especially, affords the best compromise for light-scattering experiments.

2. The rationalization of the PVF$_2$ solubility properties within the framework of a two-dimensional solubility map based on the dipole moment μ and the hydrogen-bond-accepting power β of the solvents: it may be easily used as an efficient predictive tool for the research of new functional series of good solvents.

3. A semiquantitative interpretation of chain expansion in dilute solution as measured by the intrinsic viscosity value $[\eta]$; it emphasizes the opposite contributions of cavitation effects (Hildebrand solubility parameter δ) and of polymer–solvent hydrogen-bonding (β) interactions which appear as the major factor in these very polar systems.

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