for samples prepared under carefully controlled conditions and at limited conversions, rather good agreement can be obtained with a simple scheme assuming a lower selectivity for tertiary hydrogen atoms in the process of transfer to the polymer. However, it remains much more difficult to predict quantitatively the behavior of the polymerization process if the conversion is higher than the critical value, when the steady-state conditions cease to be valid, and under subsaturation pressure. Clearly, more detailed data must be obtained before a more sophisticated simulation process can be applied.

Registry No. PVC (homopolymer), 9002-86-2.

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Microenvironment Polarity of Macromolecules in Solution and in the Condensed State. 1. Solvatochromic Approach in Dilute Solution

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ABSTRACT: Quantitative analysis of the microenvironment polarity of macromolecules in dilute solution was performed by the solvatochromic approach: The solvent effects on the transition energies E_T related to the formation of an intramolecular charge-transfer band were compared in a pyridinium dicyanomethylide chromophore $RC_5H_4N^+C^-(CN)_2$, a low molecular weight model analogue ($R = C_2H_5$), and in a probe covalently fixed on seven polymers of various structures, such as poly(methyl methacrylate), poly(dimethylacrylamide), or poly(hydroxyethyl methacrylate). The solvatochromy of both the model and the labeled polymers may be quantitatively analyzed within the framework of Taft's "linear solvation energy relationships": $E_T = E_T^\circ + s\pi^* + a\alpha$, where π^* and α are empirical polarity parameters of the solvent. Dipolar interactions (π^*) always prevail over hydrogen bonding (α), but their respective contributions are not quite identical for the model and the labeled polymers. Comparative analysis of the solvatochromic data allows an estimation of the volume fraction of solvent ϕ_s in the solvation sphere of the probe fixed to the macromolecular chains—$\phi_s = 0.55$–0.78—and of the polymer polarity defined by π^* and α. Because of restrictions of probe orientation, polymers always appear less polar than expected from the chemical structure of their lateral groups.

Introduction

It is well established that for a kinetically controlled reaction of a given reagent with a macromolecular substrate in homogeneous solution a number of factors specific to the macromolecular structure cause a difference between the polymer reactivity (kinetics and selectivity) and that of its low molecular weight model of similar structure.[1,2] Besides intramolecular neighboring-group effects, which have received much attention especially from a theoretical point of view,[3,4] the "effective local solvent medium" in the solvation sphere of the reaction site linked to the polymeric backbone may be easily identified as an important factor:[5,6] with respect to all short-range interactions that may occur in the vicinity of the reaction site, the solvent S, which constitutes the whole solvation sphere for the low molecular weight model, is in competition with the chain backbone and the neighboring groups, which contribute to define the local "microenvironment polarity" through their steric and electronic effects. Within the last decade this concept of local polarity has led to numerous and fruitful studies, but it still remains to be defined in a more quantitative way as are, for instance, solvent effects in organic chemistry.[7] This major goal is not merely of fundamental interest but also of technological importance, since a comprehensive knowledge of polymer reactivity in solution or in the swollen state (cross-linked resins) is a

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necessary prerequisite to optimize the synthesis and the use of functional polymers in many fields of increasing importance, such as polymer-supported reagents and catalysts,[8] polymeric drugs,[9] and so on. The purpose of this work is to present a general approach for the quantitative determination of the microenvironment polarity of macromolecules in solution and to check its efficiency and shortcomings at the experimental level on a series of seven polymers of different chemical structures.

Microenvironment Polarity of Macromolecules in Solution. General Methodology for Its Quantitative Determination

The general strategy rests upon the comparison of solvent effects on a well-selected solvent-sensitive physicochemical property X of a reporter species, either as a low molecular weight model compound, M, or as a probe covalently fixed to the macromolecular chain in very low amounts (~0.01 mol fraction) in labeled polymer P*. Such an approach, pioneered a long time ago by biochemists (e.g., the local dielectric constant close to the reaction site of various enzymes[10]), has also stimulated numerous studies of synthetic polymers involving different X properties, such as chemical,[11,12] photochemical reactivity,[13] tautomerism,[14] and mainly spectroscopic properties: solvatochromy and photochromism of merocyanines dyes[15-17] and solvatochromy of pyridinium phenolate zwitterions.[18,19] In spite of the interest of these earlier studies, it remains to quantify all these observations in a self-consistent framework so as to define a polarity scale for polymers and to estimate the respective contributions of the macromolecular chain and of the solvent to the polarity within the solvation sphere of the probe.

Two-Parameter Model for the Quantitative Analysis of the Microenvironment Polarity of Macromolecules in Solution Using "Linear Solvation Energy Relationships". In a first approach the local polarity π within the solvation sphere of the reporter may be quantitatively described with a two-parameter model according to

$$\pi = \phi_s \pi_s + \phi_{P*} \pi_{P*}$$

where ϕ_s and ϕ_{P*} are the volume fractions of solvent and of polymer units, respectively, in the solvation sphere ($\phi_s + \phi_{P*} = 1$) and π_s and π_{P*} are polarity parameters of the solvent and of the polymer within the same polarity scale. Determination of the parameters ϕ_s and π_{P*} rests upon the quantitative analysis of the X variations with respect to solvent polarity for the model M and for the labeled polymers P* through quantitative correlations such as

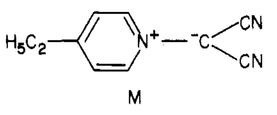
$$X_M = f(\pi_s) \quad \text{and} \quad X_{P*} = f'(\pi_s)$$

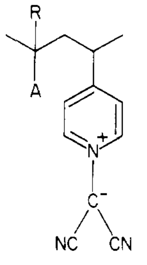
Taft et al.[20] have recently shown that any X property is best analyzed within the framework of "linear solvation energy relationships" (LSER) and may be quantified through a linear multiparametric equation according to

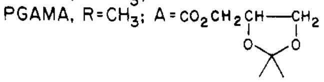
$$X = X_0 + d\delta_H + s\pi^* + a\alpha + b\beta$$

The various additive terms are specifically related to a given type of solute–solvent interactions through well-selected polarity parameters of the solvent (δ_H, π^*, α, and β). X_0 is the intrinsic value of the X property in the absence of any interaction (probe in the gaseous state for instance), δ_H is the Hildebrand solubility parameter, related to cavitation effects, π^* is an empirical polarity parameter related to dipolar interactions, and α and β are empirical parameters related to the hydrogen-bond-donating (HBD) and -accepting (HBA) power of the solvent, respectively. Fortunately, in most cases, two parameters are enough to take into account all the experimental X variations within a self-consistent framework.

Solvatochromy of Pyridinium Dicyanomethylide Chromophores as a Probe for Testing the Local Polarity. The UV spectrum of isoquinolinium ylides in dilute solution is characterized by a long-wavelength transition related to the formation of an intramolecular charge-transfer complex (ICTC) that shows a relatively strong solvatochromy,[21] and its transition energy E_T (kcal·mol^{-1}) has been quantitatively analyzed by Taft et al.[22] in terms of dipolar and hydrogen bond interactions ($E_T = E_T^\circ + s\pi^* + a\alpha$). We focus our interest on the solvatochromy of an analogous pyridinium dicyanomethylide, which allows the labeling of polymers of various structures in a very selective way. The systems under study are summarized below

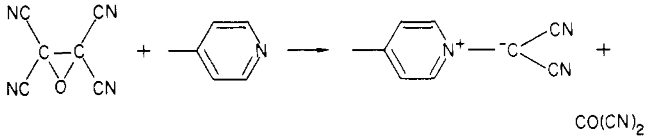

M


P*

PMMA, R = CH_3; A = CO_2CH_3
PMEMA, R = CH_3; A = $CO_2(CH_2)_2OCH_3$
PHEMA, R = CH_3; A = $CO(CH_2)_2OH$
PDMA, R = H; A = $CON(CH_3)_2$
PMAN, R = CH_3; A = CN

PGAMA, R = CH_3; A = CO_2CH_2CH—CH_2 (O–C(CH_3)$_2$–O ring)
PGMA, R = CH_3, A = $CO_2CH_2CH(OH)CH_2OH$

Results and Discussion

Synthesis of the Labeled Polymers. The key step of the reaction process is the ylide synthesis through ring opening of tetracyanoethylene oxide (TCNEO) by the pyridine moiety.[24,25]



In our hands this reaction carried out on 4-vinylpyridine (4VP) leads to a complex mixture from which we were not able to separate the ylide monomer in sufficient yield and purity. The preparation of the required polymers may be easily performed in a two-step procedure: (a) free radical copolymerization of monomer A with 4VP, and (b) quaternization of the pyridine units in the copolymer chain by TCNEO.

The first stage requires a specific comment: since the quaternization reaction is not compatible with the hydroxylic group,[26] the alcohol functions of both HEMA and GMA monomers were previously protected as trimethylsilyl ether[27] and glycol dimethyl acetal,[28] respectively, according to literature procedures. Deprotection of the labeled polymers P* in an acidic medium is selective and quantitative (see Experimental Section). All the copolymerizations were performed in a homogeneous solution at 60 °C in the presence of azobis(isobutyronitrile) (AIBN) as radical initiator. The 4VP mole fraction in the monomer feeds, f(4VP), was kept within the range 0.006–0.010 in such a way that its mole fraction in the resulting copolymers, F(4VP), never exceeds 0.020 (potentiometric

Table I
Radical Copolymerization of the Monomer Pairs A + 4VP at 60 °C[a]

A	[A + 4VP] mol·L^{-1}	f(4VP)	solvent	time, h	yield, %	F(4VP)	$\bar{M}_w \times 10^{-5}$
MMA	4.00	0.006	toluene	1.25	29.0	0.010	0.921
MEMA	3.33	0.006	toluene	1.50	40.4	0.010	2.55
GAMA	1.00	0.007	benzene	6.75	53.4	0.013	0.737[b]
MAN	6.00	0.008	DMAC	4.75	10.7	0.021	0.311
DMA	4.00	0.010	dioxane	1.0	49.9	0.008	2.49
HEMA-Si	3.55	0.006	benzene	3.0	32.0	0.007	2.78[b]

[a] In all copolymerization systems, [AIBN]/[A + 4VP] = 0.01. [b] $\bar{M}_w$ of the hydroxylated polymers derived by hydrolysis from their respective precursors.

titration with $HClO_4$ in CH_3CO_2H[29]). All the 4VP units are expected to occur as isolated units in A–4VP–A triads, without altering the A_n chain polarity. In the only case where the reactivity ratios were available—r(MMA) = 0.566, r(4VP) = 0.772[30]—it may be checked that more than 99% of the labeling probe belongs to MMA–4VP–MMA triads in our copolymer.

The quaternization step was performed in homogeneous THF solution (acetone for PMAN) at 50 °C during 5 h, using a 2.5-fold excess of TCNEO. In the determination of the quaternization yield, $HClO_4$ in anhydrous CH_3CO_2H allows the potentiometric titration of the residual 4VP units[29] but does not lead to any clear equivalence point with the model ylide M. However CF_3SO_3H diluted in CH_3CO_2H does allow the ylide titration in the binary solvent acetic anhydride/acetic acid (9/1 v/v)): one acid equivalent per zwitterion.[31] Quantitative quaternization of the 4VP units was observed for all copolymers owing to two favorable factors: (a) the very low amount of 4VP units in the labeled chains, which allows the reaction to proceed entirely in homogeneous solution (attempts to quaternize styrene/4VP or methyl methacrylate/4VP copolymers at more than 0.15 mol fraction of ylide units result in phase separation from THF solution and in inhibition of the reaction[23]), and (b) the lack of steric hindrance around the pyridine nitrogen in the 4VP structure (a quaternization of a random MMA/2-methyl-5-vinylpyridine (2M5VP) containing a mole fraction of 0.03 2M5VP units affords only a very low yield of about 10% in spite of a reaction time of 17 h, in good agreement with the very low yield of 2% already observed for the system 2-picoline/TCNEO[32]).

UV Measurements on the Model M and the Labeled Polymers P*: Reliability of the Measurements and Correlation Analysis. All the UV measurements were performed on freshly prepared solutions in order to avoid photodecomposition of the ylide.[23] The accuracy on the λ_{max} determination (repeated measurements by different experimentalists on different solutions) is generally better than ±0.2 nm. Purity of the solvents and especially their residual water content are of major importance for the reliability of the experimental results. We compare in Figure 1 the variation of λ_{max} (long-wavelength band, see further) with the water content of ethyl acetate solutions of the model M, PMMA* and PDMA* as representative hydrophobic and hydrophilic polymers, respectively. As expected PDMA* shows the highest sensitivity to water, arising probably from the strongest preferential adsorption: a water mole fraction of 0.03 is sufficient to decrease its λ_{max} from 406 to 401.3 nm, its characteristic value in pure ethanol. However λ_{max} is independent of the water concentration for mole fractions lower than 0.005 (0.05 mol·L^{-1}), and the solvents were sufficiently dried in all cases (see Experimental Section) in order to obtain reproducible and physically meaningful results.

We studied the solvatochromism of the different species in solution in a series of solvents of widely different polarities (apolar, dipolar aprotic, or protic), and the corresponding transition energies E_T (E_T (kcal·mol^{-1}) = 251 580/λ nm) were tentatively correlated with Taft's empirical polarity parameters π^* and α of the solvents: $E_T = E_T^\circ + s\pi^* + a\alpha$. The reliability of the correlation was estimated by the total regression coefficient R (n solvents) and the mean square standard deviation σ. The relative contributions of dipolar and hydrogen bonding interactions to the solvatochromy may be estimated in two complementary ways: (a) directly from the s/a ratio, *independently of the solvent population investigated*, since the π^* and α parameters are roughly normalized to cover a range from 0.0 to near 1.0,[20] and (b) from the partial regression coefficients s' and a', derived from the statistical analysis of the coefficients s and a[33] (see Appendix), which afford the respective contributions of the two terms *only for the well-defined solvent series experimentally involved.* The observed λ_{max} values and the solvent polarity parameters[20] are given in Table II.

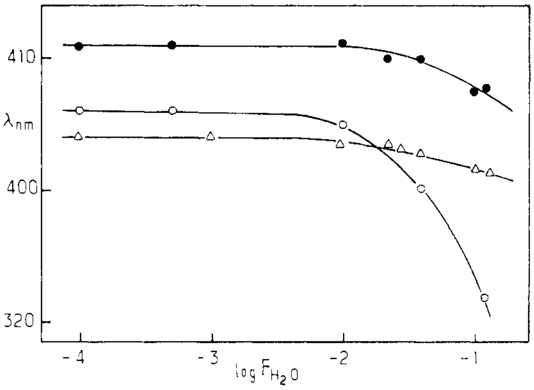


Figure 1. Influence of the water content (molar fraction f_{H_2O}) on the λ_{max} of the ICT band of pyridinium dicyanomethylides for ethyl acetate solutions of the model M (△), PMMA* (●), and PDMA* (○).

Solvatochromy of the Model 4-Ethylpyridinium Dicyanomethylide. The UV–vis spectrum of model M shows (a) a short-wavelength absorption, λ_{max} = 213 ± 1 nm, characteristic of the $\pi \rightarrow \pi^*$ transition of the pyridinium nucleus (ϵ = 15 160 L·mol^{-1}·cm^{-1} in dioxane), and (b) a long-wavelength structureless absorption resulting from an intramolecular charge transfer (ICT), whose λ_{max} decreases from 431.0 nm in tetrachloroethylene to 370.5 nm in hexafluoro-2-propanol. Beer's law checked in 2-methoxyethanol is well obeyed within a wide concentration range, 3.5 × 10^{-5}–1.3 × 10^{-2} mol·L^{-1}: self-association that could influence the ICT transition may be safely ruled out. The measurements were generally carried out at a concentration of about 5 × 10^{-4} mol·L^{-1}. In most solvents the width at half-height of the absorption band $\Delta\nu_{1/2}$ lies between 2500 and 3500 cm^{-1}, with a tendency to increase with frequency ν and thus with the medium polarity: see Figure 2. The molar absorptivity is nearly constant: ϵ = 20 400 ± 700 L·mol^{-1}·cm^{-1}.

Table II
Solvatochromic Data (λ_{max}) for 4-Ethylpyridinium Dicyanomethylide (M) and the Corresponding Labeled Polymers (P*)

	π^*	α	M	PMMA*	PMEMA*	PGAMA*	PDMA*	PMAN*	PMEMA*	PGMA*
1 diethyl ether	0.27	0	415.0							
2 *n*-butyl acetate	0.47	0	406.6	412.5	411.5	414.2	408.0			
3 1,2-dimethoxyethane	0.53	0	402.0	411.2	411.5	409.0	406.0			
4 ethyl acetate	0.55	0	403.5	410.7	409.8	412.0	406.0			
5 methyl acetate	0.56	0	400.9	409.2	408.4	410.7	405.4			
6 tetrahydrofuran	0.58	0	406.2	413.3	411.8	414.2	409.4			
7 diethylene glycol dimethyl ether	0.64	0	401.1	409.9	409.5	411.9	405.8			
8 tributyl phosphate	0.65	0							408.0	
9 cyclohexanone	0.69	0	401.2	409.1	408.0	410.0	404.8	409.3	405.3	
10 triethyl phosphate	0.72	0							404.2	404.0
11 acetic anhydride	0.76	0	395.2	404.0	403.0	405.0	400.6	405.0		401.5
12 γ-butyrolactone	0.87	0	392.3	405.5	401.0	402.0	398.4	402.1	400.2	
13 *N,N*-dimethylacetamide	0.88	0	394.9	402.8	402.8	404.0	400.5	403.5	402.4	401.2
14 *N,N*-dimethylformamide	0.88	0	393.9	402.6	402.0	403.5	399.7	402.4	401.4	401.0
15 *N*-methylpyrrolidone	0.92	0	396.0	403.5	403.5	404.5	400.5	402.1	402.5	401.5
16 tetramethylene sulfone	0.98	0	392.0	402.1	401.5	403.0	399.0	402.0	400.0	399.2
17 dimethyl sulfoxide	1.00	0	391.9	400.6	400.5	401.5	397.1	400.0	399.5	398.8
18 propylene carbonate	1.01	0	391.4	400.7	400.7	402.0	398.0	401.3	398.3	399.5
19 *tert*-butyl alcohol	0.45	0.66	394.9	406.0			403.0			
20 *n*-butyl alcohol	0.46	0.79	394.7				404.0			
21 isopropyl alcohol	0.47	0.77	393.6				402.5		400.0	
22 ethanol	0.54	0.85	392.0				401.3		400.0	
23 acetic acid	0.58	1.01	386.8	397.8	397.5	399.7	395.9		395.8	
24 methanol	0.60	0.98	387.5				398.0		397.2	396.9
25 hexafluoro-2-propanol	0.65	1.90	370.5	388.8	387.5	390.7	389.9	395.4	389.0	389.8
26 2-butanone	0.67	0.05	399.5	407.3	402.8	404.9	402.5	407.4		
27 acetone	0.72	0.10	396.7	405.6	404.5	406.5	401.5	405.7		
28 trifluoroethanol	0.79	1.35	377.7	392.4	390.0	392.5	392.0	395.4	391.5	391.0
29 acetonitrile	0.85	0.22	391.4	402.1	401.5	403.0	398.7	402.7		
30 ethylene glycol	0.85	0.92	387.4				395.4		395.5	395.0
31 water	1.09	1.10	372.3				388.8			389.4

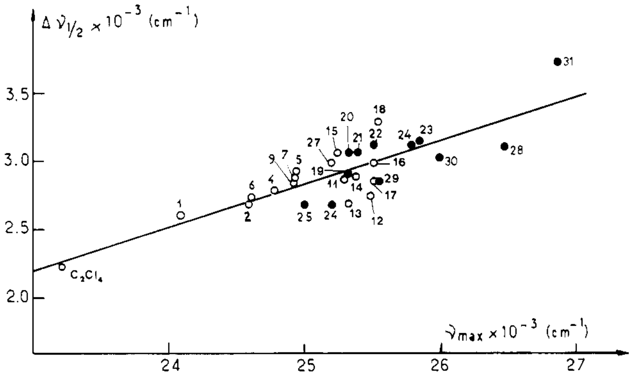


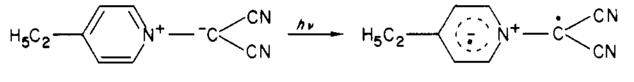
Figure 2. Variation of the width at half-height $\Delta\nu$ vs. frequency ν at maximum of the ICT band for the model M in solution in aprotic (○) or protic (●) solvents. The numbers refer to the solvent indexation of Table II.

Stepwise regression analysis on the E_T values vs. π^* and α leads to the correlation (Figure 3).

$$E_T(\mathrm{M})\ (\mathrm{kcal{\cdot}mol^{-1}}) = (67.89 \pm 0.31) + (5.17 \pm 0.41)\pi^* + (2.99 \pm 0.11)\alpha$$

$$R(29\ \mathrm{solv}) = 0.986, \qquad \sigma = 0.29$$

This good correlation may be discussed by comparison with those related to analogous isoquinolinium ylides;[22] see Table III. In all cases the *s* and *a* coefficients are positive: charge is more delocalized and hydrogen bonding is weaker in the excited than in the ground state. By analogy with the structure proposed by Kosower for pyridinium cyclopentadienylide,[34] the ICT associated with the long-wavelength transition could be described according to the following scheme:



The *a* coefficient decreases progressively with the substituent of the carbanion in the order aromatic ketone > aliphatic ketone > ester > nitrile: this decrease parallels the charge delocalization on the carbanion, and hydrogen bonding is no more the major factor of solvatochromy for the model M.

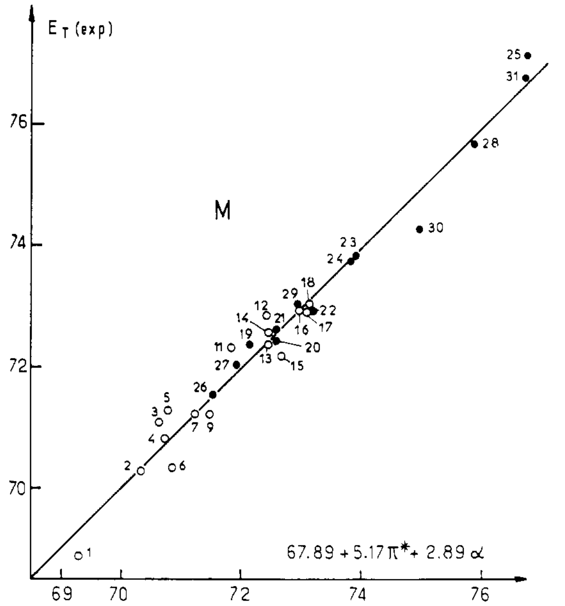
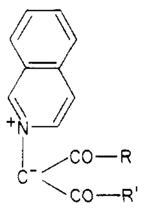


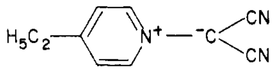
Figure 3. Experimental vs. calculated transition energies E_T (kcal·mol^{-1}) of the ICT band for the model M (same legend as in Figure 2).

Solvatochromy of the Labeled Polymers P*. Before systematic analysis of the solvatochromy, possible polymer concentration effects on the ICT transition were studied for PMMA* ($\bar{M}_w = 9.21 \times 10^4$, F(ylide) = 0.01) solutions in 2-methoxyethanol ([η] = 0.173 dL·g^{-1} at 25 °C) as a representative system. When the polymer concentration is increased from 0.053 to 10.7 g·dL^{-1}, no significant var-

Table III
Solvatochromy Correlations for Some Isoquinolinium (I) and Pyridinium (II) Ylides



I



II

nitrogen ylide			$E_T = E_T^\circ + s\pi^* + a\alpha$			
	R	R′	E_T°	s	a	$a'/(s'+a')$
I[a]	OEt	OEt	58.24	6.16	6.74	0.66
	OEt	C_6H_5	60.48	5.51	9.07	0.74
	OEt	CH_3	60.61	5.82	8.07	0.71
II			67.89	5.17	2.89	0.59

[a] Literature data:[21,22] solvents 4, 14, 17, 20–22, 24, 27, 30, n-propanol, and formamide.

iation can be observed for the λ_{max} (402.5 ± 0.2 nm), the width at half-height $\Delta\nu_{1/2}$ (2810 cm^{-1}) and for the molar absorptivity ϵ (26 150 ± 550 $L{\cdot}mol^{-1}{\cdot}m^{-1}$). The critical concentration of chain overlap C^*[44] for these polymer solutions is about 5.2 $g{\cdot}dL^{-1}$, and it may be thus concluded that there is no discontinuity in the chromophore behavior when going from dilute to semidilute solutions, as already noted for some labeled[18] or unlabeled[35] polymers. Moreover, identical transition energies are actually observed in two solvents of different thermodynamic affinity for the macromolecular chain: E_T = 71.08 $kcal{\cdot}mol^{-1}$ for PMMA* in both acetonitrile, a Θ solvent ([η] = 0.119 $dL{\cdot}g^{-1}$ at 30 °C), and in 3-methylsulfolane, a much better solvent ([η] = 0.198 $dL{\cdot}g^{-1}$ at 30 °C). This characteristic E_T independence on chain expansion or segment density within the solvated random coil clearly shows that the chromophoric probe actually tests the polarity at a very local level and that the observed solvatochromy is not perturbed by excluded volume effects. The measurements on the various polymer–solvent pairs were generally performed at a concentration of about 0.05 $g{\cdot}dL^{-1}$. The linear correlations $E_T(P^*) = E_T^\circ(P^*) + s_{P^*}\pi^* + a_{P^*}\alpha$ are given in Figure 4, and the various coefficients are collected in Table IV. Correlations are fairly good and even very good for PMMA* and PGMA*. Because of their low accuracy (about 18% as an average value, see Table IV) it seems more reasonable to arrange all the s/a ratios around three more representative values: 1.8 ± 0.2 for the model M, 2.0 ± 0.4 for PMMA*, PMEMA*, PGAMA*, PHEMA* and PGMA*, and 3.0 ± 0.4 for PMAN* and PDMA*. This suggests that the s/a ratio is actually increased with respect to its characteristic value for the model only for the two last polymers. This enhancement of the contributions of dipolar interactions with respect to that of hydrogen bonding ones may be tentatively correlated with the highest dipole moment values shown by the lateral nitrile and tertiary amide groups of PMAN* and PDMA*, respectively. However the observed s/a ratio actually increases because the a_{P^*}/a_M ratio (~0.42) decreases more than s_{P^*}/s_M (~0.73): this feature suggests that stronger restriction in hydrogen bonding interactions is the major factor of the observed behavior and that the dicyano carbanion, stabilized by dipolar interactions with its neighbors (or with solvent), is less available as an hydrogen-bond-accepting site. In any case, when sufficiently polar, the neighboring units may interact with the zwitterionic probe or its solvation shell in such a way that there is no "a priori" reason for an identical s/a ratio for the model and the labeled polymers, whatever their structures. Finally, the strongly predominant influence of the dipolar term observed in all cases probably arises from the unusually high dipole moment of the ylide probe: 9.3 D for pyridinium dicyanomethylide.[36] The model and the labeled polymers P* may be compared by combining the linear two-parameter correlations or, more directly, analyzing the variation of $E_T(P^*)$ vs. $E_T(M)$ for identical solvents. The $E_T(P^*)$ values are actually a linear function of $E_T(M)$ for every polymer, and the coefficients of the relation $E_T(P^*) = \lambda + KE_T(M)$ are given in Table V, where all the solvents are considered together or separated in non-hydrogen bonding (NHB, $\alpha = 0$) and hydrogen bond donor (HBD, $\alpha > 0$) species: variance analysis[37] shows that for most polymers the separation between NHB and HBD solvents is also statistically founded (F test positive).

Determination of the Volume Fraction of Solvent ϕ_s in the Solvation Sphere of the Probe. Straightforward calculation yields

$$\phi_s = K = s_{P^*}/s_M = a_{P^*}/a_M$$

The differences observed between the various ϕ_s values given in Tables V and VI arise partly from the differences in goodness of the various linear regressions. The too low accuracy precludes any quantitative interpretation of these calculated values, but three interesting trends are worth noting.

(a) The ϕ_s values derived from protic solvent systems are systematically lower than those derived from the aprotic ones (by an average value of about 25% if all the polymers are considered together). This feature suggests that the assumption of the independence of ϕ_s on solvent structure (e.g., self-association is stronger for protic than for aprotic species) and possibly on overall chain solvation (see further) is probably oversimplified.

(b) A critical analysis of the $\phi_s = K$ data shows that ϕ_s decreases slightly when increasing the polarity of the lateral group of the chain: considering for instance the whole solvent set, the three less polar polymers (PMMA, PMEMA, and PGAMA) are characterized by an average ϕ_s value of about 0.66 ± 0.05, significantly higher than that observed for the more polar aprotic or protic ones (PMAN, PDMA, PHEMA, and PGMA), ϕ_s = 0.51 ± 0.05, and the most polar PGMA seems to lead to the lowest ϕ_s value. Possible specific interactions between the zwitterion probe

Table IV
Solvatochromy Correlations for the Various Labeled Polymers P*

P*	$E_T^\circ(P^*)$	s_{P^*}	a_{P^*}	$R(n)$	σ	$a'_{P^*}/(s'_{P^*} + a'_{P^*})$
PMMA	67.29 ± 0.27	4.05 ± 0.35	1.87 ± 0.07	0.981(22)	0.21	0.58
PMEMA	67.56 ± 0.27	3.84 ± 0.35	1.83 ± 0.14	0.974(21)	0.26	0.57
PGAMA	67.26 ± 0.33	3.88 ± 0.42	1.69 ± 0.13	0.964(21)	0.29	0.56
PMAN	67.32 ± 0.58	4.04 ± 0.65	1.24 ± 0.03	0.976(14)	0.15	0.60
PDMA	68.38 ± 0.27	3.47 ± 0.34	1.17 ± 0.11	0.933(28)	0.24	0.49
PHEMA	67.87 ± 0.43	3.72 ± 0.49	1.69 ± 0.22	0.959(18)	0.25	0.60
PGMA	69.09 ± 0.43	2.47 ± 0.48	1.42 ± 0.08	0.992(13)	0.11	0.72

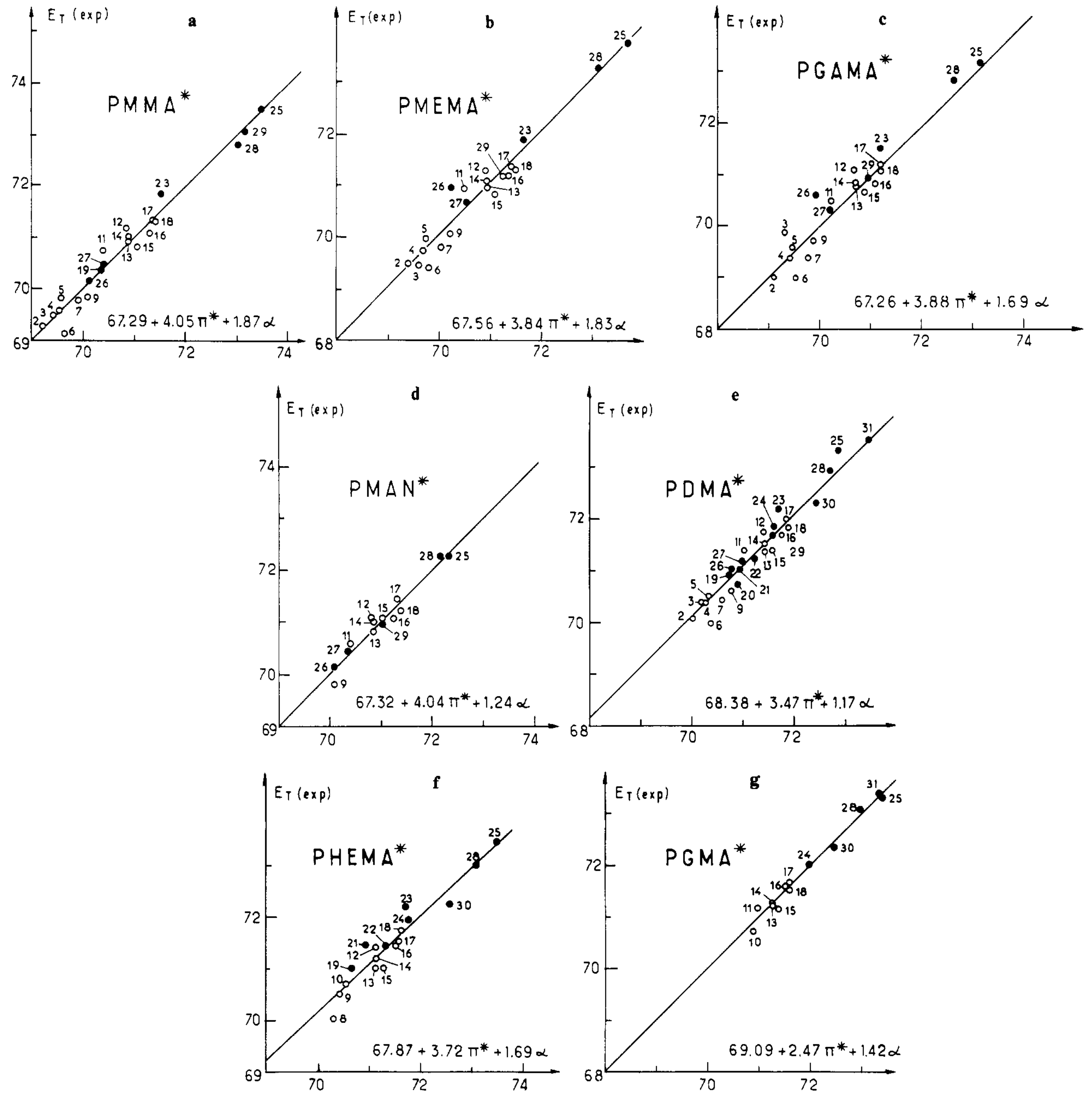


Figure 4. Experimental vs. calculated transition energies E_T (kcal·mol^{-1}) of the ICT band for the various labeled polymers: (a) PMMA*; (b) PMEMA*; (c) PGAMA*; (d) PMAN*; (e) PDMA*; (f) PHEMA*; (g) PGMA* (same legend as in Figure 2).

and the polar neighboring groups may increase the local rigidity and decrease the free volume available to the solvent. This effect could prevail over that of pure steric hindrance of the lateral groups; the ester of the glycerol 1,2-dimethyl acetal and the nitrile group, which show respectively the highest and the lowest bulkiness, do not lead to the lowest and the highest ϕ_s values for PGAMA* and PMAN*, as could have been naively expected.

(c) Finally, the volume fraction occupied by the macromolecular chain itself within the solvated random coil is only about a few percent for linear flexible polymers, and the calculated ϕ_s values which lie in the range 0.5–0.8 are thus very significantly lower than the volume fraction of solvent within the solvated random coil; the ϕ_s data are clearly related to the very local microenvironment of the probe in the labeled chain and not to the whole chain.

Determination of the Polarity Parameters of the Various Polymers. The apparent polarity parameters of a given chain may be arbitrarily identified with those of the solvent leading to the same transition energy E_T for the polymer and for the model. They may be calculated by two different ways, as in the previous case: (a) combination of the correlations E_T(P* or M) = $f(\pi^*,\alpha)$, and (b) combination of the correlations $E_T(P^*) = f[E_T(M)]$ and $E_T(M) = f(\pi^*,\alpha)$. For NHB polymers ($\alpha_{P^*} = 0$) straightforward calculation leads to

$$\pi^*_{P^*} = \frac{E_T^\circ(P^*) - E_T^\circ(M)}{s_M - s_{P^*}} = \frac{\lambda(1 - K) - E_T^\circ(M)}{s_M}$$

For HBD polymers (noted as PH*, $\alpha_{PH^*} > 0$), calculation of π^* and α parameters requires the assumption of identical π^* values for the PH* chain and its most similar homologue without the acidic hydrogen atom (noted as P* $\alpha_{P^*} = 0$): polymer pairs such as PHEMA–PMEMA and PGMA–PGAMA. This simplified approach leads to

$$\alpha_{PH^*} = \{E_T^\circ(PH^*) - E_T^\circ(M) - [E_T^\circ(P^*) - E_T^\circ(M)](s_M - s_{PH^*})/(s_M - s_{P^*})\}/a_M - a_{PH^*} = \{[\lambda_{PH^*}/(1 - K_{PH^*})] - [\lambda_{P^*}/(1 - K_{P^*})]\}/a_M$$

Table V
Correlations $E_T(P^*) = \lambda + KE_T(M)$ for the Various Labeled Polymers P*

polymers P*		all solv	NHB solv	HBD solv	F test[a]
PMMA*	λ	22.7 ± 2.2	15.1 ± 4.5	25.2 ± 2.6	
	K	0.66 ± 0.03	0.77 ± 0.06	0.63 ± 0.03	–
	$R(n)$	0.979(22)	0.959(15)	0.992(7)	
PMEMA*	λ	21.8 ± 2.3	14.6 ± 3.2	28.9 ± 4.5	
	K	0.68 ± 0.03	0.78 ± 0.04	0.58 ± 0.06	+
	$R(n)$	0.979(21)	0.979(15)	0.978(6)	
PGAMA*	λ	24.0 ± 2.5	11.7 ± 3.2	31.9 ± 4.1	
	K	0.64 ± 0.03	0.81 ± 0.04	0.54 ± 0.05	+
	$R(n)$	0.973(21)	0.981(15)	0.979(6)	
PMAN*	λ	32.5 ± 3.0	15.5 ± 9.8	31.1 ± 1.3	
	K	0.53 ± 0.04	0.76 ± 0.1	0.54 ± 0.02	+
	$R(n)$	0.966(14)	0.906(9)	0.998(5)	
PDMA*	λ	33.4 ± 2.0	19.2 ± 2.2	34.4 ± 3.0	
	K	0.52 ± 0.03	0.72 ± 0.03	0.51 ± 0.04	+
	$R(n)$	0.965(28)	0.988(15)	0.967(13)	
PHEMA*	λ	33.5 ± 1.8	25.2 ± 4.9	37.3 ± 2.3	
	K	0.52 ± 0.02	0.63 ± 0.07	0.47 ± 0.03	±
	$R(n)$	0.986(15)	0.967(8)	0.989(7)	
PGMA*	λ	36.9 ± 1.7	29.4 ± 6.4	42.3 ± 4.2	
	K	0.48 ± 0.02	0.58 ± 0.09	0.40 ± 0.05	–
	$R(n)$	0.989(12)	0.947(7)	0.973(5)	

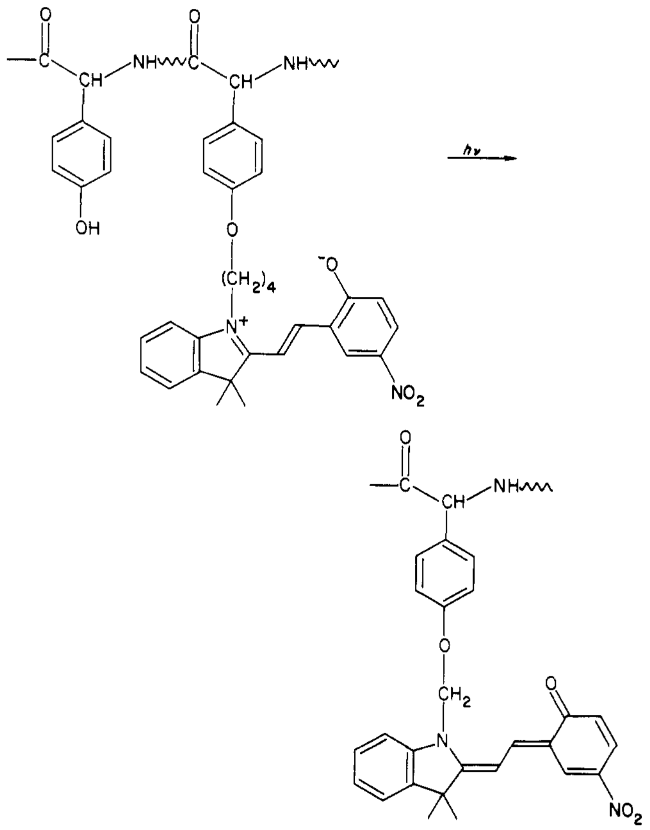
[a] F test: Separation of the solvents into two different series is statistically founded (+), not founded (–), uncertain (±).

The accuracy of the π^* and α values thus derived is indeed very low, as a result of the nonideality of the correlations involved. For instance, the large error in the $E_T°(P^*) - E_T°(M)$ term of very weak amplitude leads to a π^* range from –0.08 to +1.08 for PDMA*. Moreover the choice of correlations involving either the whole set of solvents or homogeneous series of NHB or HBD solvents remains somewhat ambiguous. All these features may explain the difference between the π^* and α values collected in Table VI for a given polymer, and these values have to be treated with caution. However, they allow some semiquantitative conclusions. The orientation restrictions imposed to the probe by its covalent linkage to the macromolecular backbone decrease its possibilities of interaction with its microenvironment and especially with its neighboring monomer units. This major factor implies three main consequences: (a) The polymer systematically appears less polar than expected from the structure of its lateral group. For instance poly(dimethylacrylamide), PDMA*, shows a most probable π^* value within the range 0.2–0.4 characteristic of ethers or ortho esters, compared to $\pi^* = 0.88$ for dimethylacetamide, its analogue. (b) For all polymers, except PGMA*, there is no common solvent such that the microenvironment polarity of the chain is more polar than that of the model; $E_T(P^*) - E_T(M)$ is always negative, and, e.g., PDMA* and PHEMA* appear less polar than the model even in apolar solvents. (c) PGMA* shows the highest polarity; it may be readily calculated that in aprotic solvents with π^* lower than about 0.44 (butyl acetate) the microenvironment of the chain is more polar than that of the model, and this feature points to the decisive contribution of the diol structure of the lateral groups to the local polarity. Finally, in an "ideal" apolar solvent ($\pi^* = \alpha = 0$), the values $E_T(P^*) = E_T°(P^*)$ would directly reflect the polarity of the macromolecular chains. The various data of Table IV may be assigned to three classes: (a) $E_T° = 67.3 \pm 0.4$ kcal·mol^{-1} for PMMA*, PMEMA*, PGAMA*, and PMAN*; (b) $E_T° = 68.2 \pm 0.4$ kcal·mol^{-1} for PDMA* and PHEMA*; (c) $E_T° = 69.1 \pm 0.4$ for PGMA*. PMAN* cannot be differentiated from the three first poly(alkyl methacrylates) in spite of the high dipole moment of the nitrile function ($\mu \sim 3.5$ D for aliphatic nitriles vs. 1.8 D for the aliphatic esters). The slightly more dipolar PDMA* ($\mu \sim 3.8$ D for aliphatic tertiary amides) and the two hydroxylated polymers definitely appear more polar, especially PGMA*: the transition energy is higher than that of the model only in this last case. All these trends are in good agreement with the rough estimation of the $\pi^*_{P^*}$ and α_{P^*} polarity parameters.

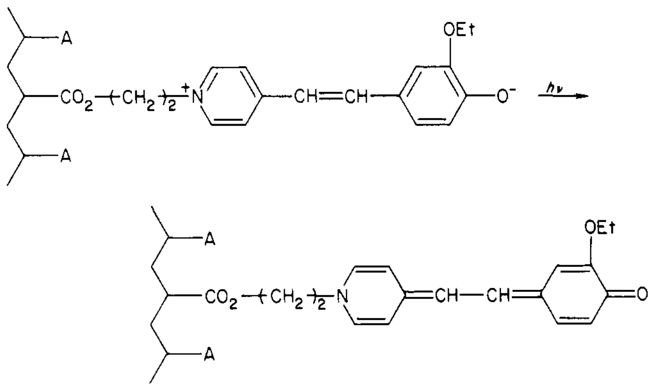
Critical Comparison with Some Related Literature Data within the Framework of the Two-Parameter Model. We have reconsidered a number of literature solvatochromic data obtained on various polymers labeled with merocyanine dyes that show a very solvent-sensitive ICT transition.[15-19] In all cases the solvent polarity was originally described by the Dimroth–Reichardt $E_T(30)$ parameter,[7] which is actually a linear combination of Taft's π^* and α parameters:[20] the good correlations we observed between the $E_T(M)$ and $E_T(30)$ values merely mean that the respective contributions of dipolar and hydrogen bonding interactions to the solvatochromy of the merocyanine model M have the same relative weights as for the reference probe of the Dimroth–Reichardt scale.[7] Direct comparison of the models and the polymers through the correlation $E_T(P)^* = f(E_T(M))$ points out the specific behavior for the various systems (Table VII). (a) For vinyl and acrylic polymers (polystyrene, poly(vinylnaphthalene), PMMA, and PMAN) labeled with 6′-nitrobenzothiazolinospiropyran[16] no statistically significant value of the solvent volume fraction ($\phi_s = K$) may be derived from the experimental data: it is difficult to assume that this failure is due only to the relatively high chromophore content of the polymers (mole fraction 0.09–0.13), which may induce intramolecular probe–probe interactions. (b) For poly(1-tyrosine) labeled with indolinospirobenzopyran (mole fraction 0.277),[17] experimental data obtained in only five solvents poorly correlate to afford a $\phi_s = K$ value of 0.19 ± 0.06 for the higher wavelength band: this very low figure, which reflects very weak variations of probe solvation, is surprising in view of the $(CH_2)_4$ spacer between the chromophore and the macromolecular chain; here again the high content of the label is probably an unfavorable factor, together with problems arising from the whole chain solvation.[17]

Table VI
ϕ_s and Polarity Parameters $\pi^*_{P^*}$ and α_{P^*} for the Various Labeled Polymers P*

	correlations $E_T = f(\pi^*,\alpha)$				correlations $E_T(P^*) = f[E_T(M)]$ and $E_T(M) = f(\pi^*,\alpha)$					
	ϕ_s				$\pi^*_{P^*}$			α_{P^*}		
P*	s_{P^*}/s_M	a_{P^*}/a_M	$\pi^*_{P^*}$	α_{P^*}	all solv	NHB solv	HBD solv	all solv	NHB solv	HBD solv
PMMA*	0.78 ± 0.13	0.64 ± 0.05	–0.54	0	–0.14	–0.53	–0.03	0	0	0
PMEMA*	0.74 ± 0.13	0.63 ± 0.06	–0.25	0	–0.06	–0.48	0.26	0	0	0
PGAMA*	0.75 ± 0.13	0.58 ± 0.06	–0.49	0	–0.13	–0.93	0.18	0	0	0
PMAN*	0.78 ± 0.19	0.43 ± 0.07	–0.50	0	0.21	–0.41	0.10	0	0	0
PDMA*	0.67 ± 0.12	0.42 ± 0.05	0.28	0	0.40	0.17	0.39	0	0	0
PHEMA*	0.72 ± 0.15	0.59 ± 0.04	–0.25	0.27	–0.06	–0.48	0.26	0.58	0.60	0.54
PGMA*	0.48 ± 0.13	0.49 ± 0.05	–0.49	2.19	–0.13	–0.93	0.18	1.49	2.91	0.40



(c) The results of Kālal et al.[18] on various polymers labeled with minute amounts of betaines of the pyridinium phenolate type (mole fraction less than 0.001) are of special interest.



The thorough study of poly(4-vinylpyridine) (P4VP*) shows that it is statistically meaningful to separate protic from aprotic solvents where the solvent volume fractions K are 1.0 (0.93 for poly(2-vinylpyridine)) and 0.53, respectively: in protic solvents, which are best for poly(vinylpyridines), the variations of probe solvation are identical for the model and the labeled polymers where the chromophore is probably sufficiently distant from the macromolecular backbone to experience the same solvation as the analogue. It should be emphasized that this trend is opposite of that previously observed for PMMA*, where K decreases slightly from 0.77 to 0.63 when passing from aprotic to protic media. This characteristic feature stresses the possible influence of the solvation of the whole chain: it is not consistent with our previous remark on the insensitivity of the solvatochromy on chain expansion, and we have no explanation for this discrepancy. Comparison of the data on PMMA* is restricted to aprotic solvents: the K decrease from 0.77 to 0.30 when going from the ylide to the betaine probe is quite puzzling, but the reliability of such a very low value is questionable (only three solvents in Kalal's measurements[18]).

Table VII
Correlation $E_T(P^*) = \lambda + KE_T(M)$ for Some Polymers Labeled with Merocyanine Dyes

P*	solv	λ	K	R(n)	π^{*e}
poly(1-tyrosine)[17 a]	all solv	41.4 ± 3.2	0.19 ± 0.06	0.864(5)	
PV4P[18 b]	all solv	16.9 ± 1.9	0.62 ± 0.04	0.978(13)	0.50
	NHB solv	21.0 ± 2.0	0.53 ± 0.04	0.987(6)	0.53
	HBD solv	-2.88 ± 3.3	1.00 ± 0.06	0.992(6)	
PV2P[18 c]	HBD solv	1.83 ± 0.96	0.93 ± 0.02	0.999(3)	-1.5
PMMA[18 d]	NHB solv	32.4 ± 0.63	0.30 ± 0.01	0.999(3)	0.69

[a] Solvents 6, 14, 27, 30, and pyridine. [b] Solvents 14, 17, 19–22, 24, 26, *n*-propanol, benzyl alcohol, nitromethane, pyridine, and 2-, 3-, and 4-methylpyridines. [c] Solvents 21, 22, and 24. [d] Solvents 14, 26, and nitromethane. [e] For the model betaine used by Kalal et al.[18] $E_T(M) = 39.86 + 9.14\pi^* + 8.52\alpha$, according to Taft et al.[20]

Conclusion

The solvatochromic method used to quantify the local polarity of the microenvironment of macromolecules in solution clearly shows definite advantages but also some shortcomings.

(a) The straightforward labeling of polymers, the high sensitivity of the ylide probe, and the simplicity and accuracy of the UV measurements are strong arguments in favor of this approach.

(b) The systematic use of the "linear solvation energy relationships" developed by Taft et al.[20] allows the rationalization of the experimental data for the model and the labeled polymers in a self-consistent framework: the estimation of the respective contributions of dipolar (π^*) and hydrogen bonding (α) interactions to the observed solvatochromy provides a quantitative analysis of solvation effects at a molecular level. Moreover the linear two-parameter correlation, $E_T = E_T^\circ + s\pi^* + a\alpha$, is a reliable predictive tool.

(c) The two-parameter model we proposed to compare the polymer and its analogue is probably oversimplified, but it allows some important semiquantitative conclusions: the volume fraction of the probe solvation sphere accessible to the solvent, ϕ_s, lies within the range 0.5–0.8 for all investigated polymers, and it is greater by about 38% for aprotic as compared with protic solvents. Analysis of the expected variations with chain structure would require the study of well-defined systems (increase of the steric hindrance of the polymer lateral group without changing too much its polarity, in the poly(alkyl methacrylate) series, for instance) and an improvement of the accuracy of the linear correlations which may be reasonably expected from the continuous optimization of Taft's π^* and α parameters.[39] The strong restriction to probe orientation is the major factor in the apparent low polarity of the macromolecular chains; although the $\pi^*_{P^*}$ and α_{P^*} parameters are only rough estimates, the order of polymer polarities shows the trend expected from their chemical structure. More reliable $\pi^*_{P^*}$ and α_{P^*} values could be derived from the solvatochromy of glassy polymeric films doped with minute amounts of the model probe (homogeneous blends P + M).[40]

(d) Comparison of our results with some related literature data shows that the microenvironment polarity of a given chain in solution may be strongly dependent on the labeling probe (structure, possible spacer between the probe and the macromolecular backbone) and that overall coil solvation effects may interfere with the very local solvation.

When studying the local polarity of binding sites of proteins, Kosower et al.[43] already noticed that probably "no useful unique polarity can be measured", but we believe that an optimized solvatochromic approach using Taft's methodology may yield quantitative and reliable results in a field that remains of major importance for an analysis of macromolecule reactivity in solution.

Experimental Section

Physical Measurements. UV spectra were run at room temperature on a Beckman Acta V or on a UV-240 Shimadzu spectrometer. Whenever necessary, the optical lengths of the various cells ($l < 0.1$ cm) were checked with standard potassium chromate solutions.[42] Specific refractive index increments, dn/dc, were determined at room temperature on a differential Brice Phoenix BP-10004 refractometer: dn/dc in DMF (for λ = 5460 Å) = 0.055, 0.088 and 0.076 mL·g^{-1} for PMEMA, PMAN, and PHEMA, respectively; dn/dc in CH_3OH (for λ = 6320 Å) = 0.194 and 0.166 mL·g^{-1} for PDMA and PGMA, respectively; dn/dc in THF (for λ = 5460 Å) = 0.143 mL·g^{-1} for PGAMA. Weight-average molecular weights were derived from light scattering measurements on a Fica PGD-420.04, and intrinsic viscosity measurements were carried out on an automatic Fica viscosimeter. Potentiometric titrations were performed on a Metrohm-436 device fitted with the EA-121 glass–calomel electrode, using the following experimental conditions: $HClO_4$ in AcOH as titrating reagent and AcOH, acetonitrile or 2-propanol/glycol (1/1 (v/v)) as solvents for the determination of 4VP units in the various copolymers;[29] CF_3SO_3H in AcOH as titrating reagent and Ac_2O/AcOH (9/1 (v/v)) as solvent for the pyridinium dicyanomethylide functions[31] (titration under argon in the latter case).

Solvents, Monomers, and Reagents. In some cases the solvents of the best "spectrophotometric grade" were used as received (CH_3OH, Ac_2O, trifluoroethanol), but most often they were purified according to literature methods by distillation over suitable drying reagents[43] (disodium benzophenone dianion for ether solvents, H_2Ca for tertiary amide, sulfoxide, and ester solvents, P_2O_5 for CH_3CN) and stored under argon over molecular sieves 4A or 3A. Water determinations by Karl–Fisher titration carried out at random on a few solvents showed that the residual water content never exceeded 10 ppm. The commercially available monomers were purified by distillation over H_2Ca just before polymerization. (Trimethylsilyl)ethyl methacrylate[27] and (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate[28] were synthesized and purified according to literature. TCNEO was prepared by oxidation of tetracyanoethylene with *tert*-butyl hydroperoxide:[24] the crystallized reagent may be stored in the dark at −20 °C for several months without any decomposition. AIBN was twice crystallized from toluene solution.

Synthesis of the Model, Polymerizations, and Polymer Functionalization. All the syntheses were carried out under a slight pressure of argon in an all-Pyrex-glass reactor after previous vacuum and argon sweeping cycles. Solvents and reagents were introduced under argon from Schlenk vessels or through self-sealing rubber caps using syringe technique.

Ethylpyridinium Dicyanomethylide (Model M). Quaternization of 4-ethylpyridine by TCNEO was carried out by the literature procedure for pyridine:[24,25] mp 171 °C; basicity equivalent (CF_3SO_3H as titrating reagent) 0.98; UV, see text. Anal. Calcd for $C_{10}H_9N_3$: C, 70.16; H, 5.30; N, 24.54. Found: C, 69.83; H, 5.49; N, 24.97.

Radical copolymerizations and copolymer quaternizations by TCNEO (reaction vessel protected from light by aluminum foils in the latter case) were carried out in homogeneous solution as detailed in the text. The copolymers were recovered and purified by two successive precipitations, and their purity was checked by thin-layer chromatography on silica gel (Merck DC Plastifolien Kieselgel 60 F 254, R_F(TCNEO) = 0.87 for AcOEt as eluting solvent). Deprotection of the OH masked functions in 1 N HCl according to literature is selective and quantitative:[28] in our hands partial cross-linking may occur during the recovery process (intermolecular etherification catalyzed by H^+?), and previous elution of the acidic solutions on a strongly basic Merck III resin avoids any side reaction.

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Appendix

Calculation of the partial regression coefficients s' and a'[63]

$$s' = s\left[\frac{\sum_{i=1}^{n}(\pi_i{}^* - \bar{\pi}^*)^2}{\sum_{i=1}^{n}(E_{\mathrm{T},i} - \bar{E}_T)^2}\right]^{0.5}$$

$$a' = a\left[\frac{\sum_{i=1}^{n}(\alpha_i - \bar{\alpha})^2}{\sum_{i=1}^{n}(E_{\mathrm{T},i} - \bar{E}_{\mathrm{T}})^2}\right]^{0.5}$$

Where $\pi_i{}^*$, α_i, and $E_{\mathrm{T},i}$ are the values of π^*, α, and E_{T} in a given solvent i, and $\bar{\pi}^*$, $\bar{\alpha}$, and $\bar{E}_{\mathrm{T}}$ are the average values of these quantities for the given data set related to n solvents.

Registry No. TCNEO, 3189-43-3; (MMA)·(4VP) (copolymer), 26100-41-4; (MEMA)·(4VP) (copolymer), 100243-83-2; (GAMA)·(4VP) (copolymer), 100243-81-0; (MAN)·(4VP) (copolymer), 32879-52-0; (DMA)·(4VP) (copolymer), 100243-82-1; (HEMA-SI)·(4VP) (copolymer), 36180-84-4; 4-ethylpyridinium dicyanomethylide, 83799-27-3; diethyl ether, 60-29-7; *n*-butyl acetate, 123-86-4; 1,2-dimethoxyethane, 110-71-4; ethyl acetate, 141-78-6; methyl acetate, 79-20-9; tetrahydrofuran, 109-99-9; diethylene glycol dimethyl ether, 111-96-6; tributyl phosphate, 126-73-8; cyclohexanone, 108-94-1; triethyl phosphate, 78-40-0; acetic anhydride, 108-24-7; γ-butyrolactone, 96-48-0; *N*,*N*-dimethylacetamide, 127-19-5; *N*,*N*-dimethylformamide, 68-12-2; *N*-methylpyrrolidone, 872-50-4; tetramethylene sulfone, 126-33-0; dimethyl sulfoxide, 67-68-5; propylene carbonate, 108-32-7; *tert*-butyl alcohol, 75-65-0; *n*-butyl alcohol, 71-36-3; isopropyl alcohol, 67-63-0; ethanol, 64-17-5; acetic acid, 64-19-7; methanol, 67-56-1; hexafluoro-2-propanol, 920-66-1; 2-butanone, 78-93-3; acetone, 67-64-1; trifluoroethanol, 75-89-8; acetonitrile, 75-05-8; ethylene glycol, 107-21-1; water, 7732-18-5; 4-ethylpyridine, 536-75-4.

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Solvation of Hydrocarbons by Aromatic Solvents: Origin of the Doubling of the Methylene ^1H Envelope for Long-Chain Hydrocarbons in 1-Chloronaphthalene

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ABSTRACT: Heteronuclear (^{13}C–^1H) shift-correlated two-dimensional NMR spectra are used to investigate aromatic solvent induced shifts (ASIS) for straight-chain hydrocarbons in 1-chloronaphthalene. All ^1H chemical shifts can be assigned. The pattern of ASIS demonstrates that the previously noted doubling of the methylene envelope for long-chain hydrocarbons in this solvent reflects subtle differences in solvation rather than slow gauche–anti interconversions. The ability of this 2D experiment to extract accurate ^1H chemical shifts from a complex spectral envelope makes it particularly useful for investigations of macromolecules.

A number of years ago, Liu observed that the methylene envelope in the ^1H spectrum of long-chain ($>C_{16}$) hydrocarbons is split into a doublet in 1-chloronaphthalene.[1] A number of subsequent publications have attempted to provide an explanation for this observation.[2-7] The most thorough investigation has been carried out by Ando and co-workers, who concluded, mainly on the basis of ^1H chemical shift calculations, that the second peak arose from an increased number of gauche conformations for long-chain hydrocarbons in 1-chloronaphthalene.[3,4] However, there are very serious problems with this explanation. For example, the methylene doublet is still observed at 120 °C. This indicates a barrier to gauche–anti conformer interconversion of at least 120 kJ mol^{-1}, far higher than any known barrier for C–C bond rotation.[6] Furthermore, the ^{13}C spectra for long-chain hydrocarbons in 1-chloronaphthalene are almost identical with those observed in $CDCl_3$.[6] If long-lived (on the NMR time scale) gauche conformers are present in 1-chloronaphthalene, one might expect to see two distinct ^{13}C peaks for each CH_2 group, due to the well established gauche γ shielding effect.[8] Finally, it has been observed that the low-field component of the ^1H doublet increases in relative area with increasing chain length.[2,6] However, rotational isomeric state calculations indicate a negligible variation in gauche–anti ratio with chain length for hydrocarbons longer than pentane.[9] These and other similar observations led us to conclude that the methylene doublet actually reflected different solvent (ring-current) effects on internal CH_2 groups and those near chain ends.[6] However, Ando et al. have recently reiterated their arguments in favor of persistent gauche conformations, supported by results of variable-pressure ^1H NMR measurements.[10]

Since the origins of this phenomenon are still in dispute almost 20 years after its initial observation, we decided to carry out an experiment that should provide a definitive explanation for the doubling of the methylene ^1H envelope. Heteronuclear shift-correlated two-dimensional NMR spectra allow simultaneous determination of ^{13}C and ^1H chemical shifts for directly bonded ^1H–^{13}C pairs.[11] Due to the greater ^{13}C chemical shift dispersion, this should allow one to extract from the methylene envelope the ^1H chemical shift(s) of each CH_2 group. This should either reveal two distinct ^1H chemical shifts for each CH_2 group,

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