# Polyelectrolytes of High Charge Density in Organic Solvents. Synthesis and Viscosimetric Behavior

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ABSTRACT: An easy anion exchange between electrolyte monomers of the quaternary ammonium halide type such as [(2-methacryloyloxy)ethyl]trimethylammonium chloride or 1-vinyl-3-methylimidazolium iodide and various cyanocarbon salts such as 1,2,2-tricyanoethenolate, 1,1,2,3,3-pentacyanopropenide, α,α-dicyano-*p*-toluoylcyanide, or *p*-(tricyanovinyl)phenyldicyanomethide readily leads to a series of new hydrophobic electrolyte monomers with yields generally over 70%. [(2-Methacryloyloxy)ethyl]trimethylammonium 1,1,2,3,3-pentacyanopropenide is a most representative example. Its free radical polymerization in homogeneous solution (DMF, 60 °C) currently yields atactic chains (Bernoulli stereopropagation process, probability of meso placement $P_m = 0.31$) of fairly high degree of polymerization ($DP_w \sim 1600$) which show an unique spectrum of solubility in dipolar organic solvents (dipole moment $\mu > 2.6$ D) covering a very broad range of dielectric constants ($\epsilon \sim 10-180$). Viscosity measurements performed in 13 solvents allow us to analyze the polymer solution properties in three different situations: (a) For good, but weakly dissociating solvent (triethyl phosphate, $\epsilon \sim 10$), there were no polyelectrolyte effects. (b) For good and fairly to highly dissociating solvents (cyclopentanone...2-cyanopyridine, $\epsilon \sim 13-90$), as a general trend, polyelectrolyte effects increase with the dielectric constant, but the usual excluded volume effects remain a factor of the number of effective charges per chain, as estimated from the ratio A/B of the parameters of the Fuoss equation in its simplified form ($\eta_{red} = A/1 + BC^{0.5}$). (c) For very poor but very strongly dissociating solvents (formamide, *N*-methylformamide, $\epsilon > 100$), there were no polyelectrolyte effects at 25 °C and transition to a fairly good solvent at about 50 °C with simultaneous emergence of weak polyelectrolyte effects. These new hydrophobic polyelectrolytes appear as optimized and versatile models for the quantitative analysis of the influence of the usual excluded volume effects and of the specific electrostatic interactions on the static and dynamic solution properties of polyelectrolytes in all possible solvation and dissociation situations.

## Introduction

Since the early days of polymer science the study of natural and synthetic polyelectrolytes in solution has remained a fascinating and not yet completely understood research field of outstanding importance from a variety of fundamental, technological, and biological points of view. With respect to nonionogenic polymers, the statistical physics of polyelectrolyte solutions are definitely much more complex, because of the superposition of the usual short-range interactions (excluded volume effects) and of the long-range Coulombic interactions arising from the typical macroion−counterion dissociation in a medium of high enough dielectric permittivity.[1−7] Because of its very specific structure and ion-solvation properties and of its unique importance in life sciences, water (dielectric constant $\epsilon$ (25 °C) = 78.36) has been per excellence the polar solvent in most studies of polyelectrolyte solutions. Organic solvents have comparatively received much less attention despite their doubtless potential interest, but some general trends of polyelectrolyte behavior in these media are however already well-ascertained.[8,9] Three main cases may be clearly differentiated, as briefly outlined below.

(a) In apolar solvents such as toluene, tetrahydrofuran, and dioxane ($\epsilon < 10$), where ionic dissociation is not significant, solubility is generally observed only for chains of low charge density, such as the so-called ionomers (molar fraction of ionogenic units < 0.20) or the halato-telechelic polymers. Inter- and intramolecular clustering of the ion pairs by strong dipole−dipole interactions in these nonsolvating media systematically occurs:[8−10] These ionic associations are the major factor of all the static and dynamic properties of these systems, such as for instance the technologically important shear-thickening effects.[11]

(b) In polar protic or aprotic solvents such as alcohols or alcohol−water mixtures and dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) ($\epsilon \sim 20-50$), significant ionic dissociation obviously occurs and results in a classical polyelectrolyte-like behavior whatever the charge density of the chain is: it is observed for homopolymers[12,13] as well as for copolymers[10] and even in the limiting case of telechelic polymers bearing only one or two ionogenic end groups.[8−10]

(c) Finally, the very scarce experimental results related to polar solvents of extremely high dielectric constant, and more especially much higher than that of water, deserve special attention. No polyelectrolyte behavior could be observed in solutions of statistical anionic acrylamide copolymers (molar fraction of charged sites in the range 0.15−0.70) in formamide (F, $\epsilon$(25 °C) = 108.03) or in water−formamide mixtures (water volume fraction < 0.5).[14] Similar results were recently reported for Nafion 117 (perfluorosulfonated ionomer with a molar fraction of lithium sulfonate of 0.13) in formamide or *N*-methylformamide (MF, $\epsilon$(25 °C) = 182.4).[15] Till now no completely satisfactory explanation has been advanced both for the very low values of the reduced viscosities and for the lack of any polyelectrolyte effects in these solvents where ionic dissociation should be maximum.

Polyelectrolyte homopolymers showing simultaneously two apparently incompatible characteristics, such as a

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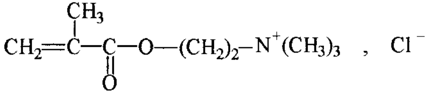
high charge density and a very broad spectrum of organic solvents of strongly different polarities, may be thus considered as optimized models for a more comprehensive analysis of polyelectrolytes in solution. Classical excluded volume effects and specific long-range Coulombic interactions could potentially be finely tuned and studied on the same chemically homogeneous homopolymer (which avoids potential problems arising from the amphiphilic character of most copolymers) considered in a series of solvents of different solvation affinity for the chain and dissociating power. Cationic poly(soaps), resulting for instance from homopolymerization of *N*,*N*-dimethylaminoethyl methacrylate[16] or 1-vinylimidazole[17] quaternized by long-chain alkyl bromides or the more recently introduced stoichiometric polyelectrolyte−surfactant complexes,[18] such as poly(*n*-alkyltrimethylammonium styrenesulfonate) for instance, meet these requirements. Their behavior in some solvents typical of the two first series (a and b) previously considered is very representative, as shown for instance by the lack of any polyelectrolyte effect in chloroform ($\epsilon(25\ °C) = 4.71$). However their strong amphiphilic character may induce complex behavior in systems involving highly dipolar solvents of very strong cohesive energy density, as a result of the solvent−paraffin incompatibility: this could be a significant drawback for the most polar solvents of series b (DMSO, etc.) and even more for the solvents of series c (self-association of the long paraffinic chains?). Two main topics will thus be successively addressed in this paper: first, the synthesis of a series of new cationic polyelectrolytes showing all the required solubility properties and, second, a first approach to the dilute solution properties of a representative polymer in a series of salt-free organic solvents covering a very broad range of dielectric permittivity ($\epsilon \sim 10-180$): viscosity measurements afford a sensitive technique for the detection of a polyelectrolyte-like behavior (typical upturn of the $\eta_{sp}/c = f(c)$ variations at low concentration) arising from intra- and intermolecular electrostatic interactions, even for very low fractions of effective charge (dissociated ion pair) per chain.

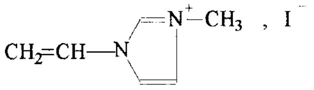
**Chart 1**

**- Precursor monomers ($N^+$, $X^-$)**



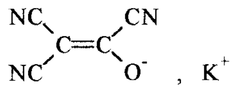
$CH_2{=}C(CH_3){-}C({=}O){-}O{-}(CH_2)_2{-}N^+(CH_3)_3\ ,\ Cl^-$

[(2-methacryloyloxy-)ethyl]trimethylammonium chloride **(M-Cl)**

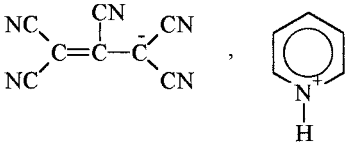


3-methyl-1-vinylimidazolinium iodide[20] **(VI-I)**

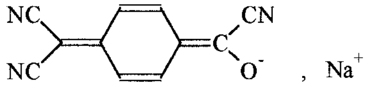
**- Precursors cyanocarbon salts ($CC^-$, $Me^+$)**



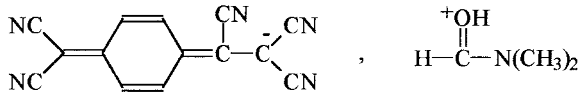
1,2,2-tricyanoethenolate [21,22] **(TCE)**



1,1,2,3,3-pentacyanopropenide [21,23] **(PCP)**



α,α-dicyano-*p*-toluoylcyanide [24] **(TCQ)**



*p*-tricyanovinylphenyldicyanomethide [25] **(PCQ)**

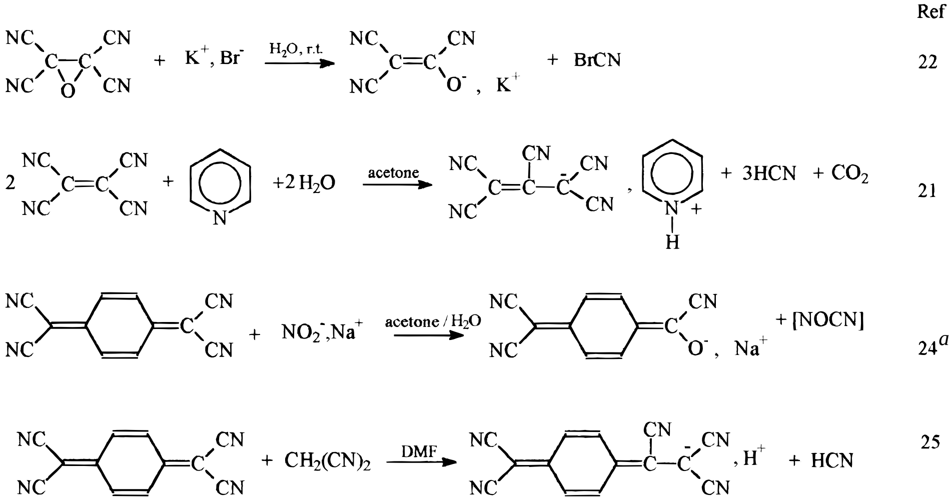
## Results and Discussion

**Monomer Synthesis.** The synthetic strategy toward a polyelectrolyte of enhanced solubility in organic solvents rests upon the free radical polymerization of an electrolyte monomer which associates a polymerizable quaternary ammonium cation with a highly delocalized organic anion derived from the cyanocarbon acids.[19] These monomers are directly obtained by methathesis (ion exchange) between a precursor monomer of the ammonium halide type ($N^+,X^-$) and a cyanocarbon salt ($CC^-,Me^+$) in purely aqueous or aqueous organic solution:

$$N^+,X^- + CC^-,Me^+ \rightarrow N^+,CC^-\downarrow + X^-,Me^+$$

The insolubility of the target monomer ($N^+,CC^-$) shifts the equilibrium quantitatively to the right. The precursor monomers and cyanocarbon salts are given in Chart 1. The easily prepared 3-methyl-1-vinylimidazolium iodide[20] (VI-I) shows a higher cationic charge delocalization than the technologically important [(2-methacryloyloxy)ethyl]trimethylammonium chloride (M-Cl). The cyanocarbon salts were derived from tetracyanoethylene (TCNE), tetracyanoethyleneoxide (TCNEO), or 7,7,8,8-tetracyanoquinodimethane (TCNQ) according to straightforward reactions mainly pioneered 40 years ago by Du Pont chemists: see Scheme 1. In most cases, the initial cyanocarbon species do not need to be isolated and the ion exchanges with the precursor monomers carried out in situ lead to the target pure monomers with overall yields with respect to TCNE, TCNEO, or TCNQ generally higher than 70% (see Experimental Section). All these crystalline monomers are best characterized by the specific spectroscopic features of their cyanocarbon anions. In infrared spectroscopy, the most typical strong absorption corresponding to the $\nu$(C≡N) vibration occurs around 2200 $\text{cm}^{-1}$, as a double peak at 2185−2215 $\text{cm}^{-1}$ for TCE, as a sharp peak at 2198 $\text{cm}^{-1}$ with weak shoulders at 2235 and 2150 $\text{cm}^{-1}$ for PCP, as a well-separated doublet at 2174−2128 $\text{cm}^{-1}$ for TCQ, and as a broad peak at 2187 $\text{cm}^{-1}$ with two strong shoulders at 2210 and 2161 $\text{cm}^{-1}$ for PCQ. Detailed IR and Raman analysis of the TCE and PCP anions may be found in the literature.[26−28] The UV spectra of the monomers in acetonitrile solution show the expected strong batochromic shift of the long-wavelength $\Pi-\Pi^Q$ transition when increasing conjugation[19] from TCE ($\lambda_{max} = 297$ nm) to PCP ($\lambda_{max} = 396$, 414 nm: two maxima of nearly identical intensity;

**Scheme 1. Synthesis of the Cyanocarbon Species**



[a] Overall reaction (detailed mechanism not precise).

bright yellow), to TCQ ($\lambda_{max} = 480$ nm, dark orange), and finally to PCQ ($\lambda_{max} = 643$ nm: very flat maximum over about 20 nm probably masking two very close bands; dark blue): see Experimental Section. The $^{13}C$ and $^{1}H$ NMR data (for TCQ and PCQ) typical of the various cyanocarbon anions are given in Table 1. They are in good agreement with previous literature data for TCE and PCP,[27] and they have been checked by 2D NMR experiments for TCQ (heteronuclear chemical shift correlation, $^{13}C/^{1}H$). Finally the $^{1}H$ NMR spectra of the monomers essentially characterize their polymerizable cations: see Experimental Section and literature for a detailed analysis of the 3-methyl-1-vinylimidazolium cation,[17,20] for instance.

**Free Radical Polymerization.** It has been performed in homogeneous solution in DMF at 60 °C, in the presence of azobis(isobutyronitrile) as initiator. The experimental results given in Table 2 suggest the following comments:

(a) For the three methacrylates M-TCE, M-PCP, and M-TBP (tetraphenylboride as anion, see further discussion), polymerization led to a fairly high degree of polymerization ($DP_w > 10^3$) with yields over 75%. Assuming in a rough approach that the variations of the initiator efficiency and of the polydispersity of the polymers are negligible within a wide conversion range, Tobolsky's calculations[29] reduce, in the case of constant polymerization time, to a simple correlation between the weight average degree of polymerization, the initial monomer and initiator concentrations, and the monomer conversion $\alpha$:

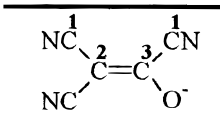
$$DP_w = K[M]_0\alpha[I]_0^{-1} \tag{2}$$

The experimental data actually lead to a constant $K$ value, $K = 9.4 \pm 0.5$: the polymerization thus appears, as expected, to be insensitive to the anion structure. The tacticity of the polyelectrolyte P(M-PCP) was derived from the analysis $\alpha$-$CH_3$ pattern of the $^{1}H$ NMR spectrum (DMSO-$d_6$, 120 °C, 200 MHz). The resonance peak assignment was directly transposed from that previously assumed for a polyzwitterion of closely related structure P(Z),[30] poly[(2,2-dicyano-1-(2-(2-(methacryloyloxy)ethyl)dimethylammonio)ethoxy)ethenolate]. The spectrum given in Figure 1 shows that only partialand poor resolution into the various pentads was achieved, and analysis was thus restricted to the triad level. According to the experimental data given in Table 3, the polymer tacticity may be fairly well-described according to Bernoulli statistics with a characteristic probability of meso placement $P(m) = 0.312$. For identical free radical polymerization conditions (60 °C, homogeneous solution) the tacticities of the homologous polyelectrolyte P(M-Cl) and of the polyzwitterion P(Z) also obey a Bernoulli stereopropagation model with very close $P(m)$ values: see Table 3. The higher steric hindrance provided by the common bulky quaternary ammonium site in these similar methacrylates is obviously the major driving force for the increase of the $P(m)$ value with respect to that of methyl methacrylate,[31] $P(m) = 0.212$. However, the lack of any significant difference between the electrolytes (free ions likely present in the dissociating solvents used for polymerization) and the zwitterionic monomer (covalent bonding between the anionic and cationic sites) is worth being stressed.

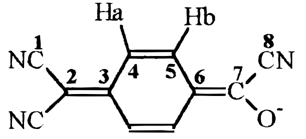
(b) For the two other methacrylates, the polymerization performed under similar conditions leads to a much lower conversion in the case of M-TCQ and does not occur for M-PCQ even for a [initiator]/[monomer] molar ratio as high as 0.02 (see Table 2): the reason for this general trend toward poor polymerizability and the difference observed between analogous monomers involving two anions of fairly similar structure remains to be elucidated. Some quinodimethanes bearing two different electron-accepting substituents at positions 7 and 8 are known to homopolymerize through a radical mechanism,[32] and the TCQ and PCQ anions of related mesomeric structure may perhaps interfere with the free radical processes.

(c) In the 1-vinylimidazolium series, the degree of polymerization obtained for the VI-PCP monomer is weak, $DP_w \sim 80$, and lower by a factor of about 20 than that obtained for the homologous methacrylate under similar conditions. The choice of a less polar polymerization solvent could perhaps lead to higher molecular weights, as already observed for polymerizable cationic surfactants of the quaternary ammonium methacrylate[16] or 1-vinylimidazolium [17]type. VI-PCQ does not polymerize: this failure is self-consistent with that of the homologous methacrylate and it re-emphasizes the potential inhibition role of the PCQ counterion.

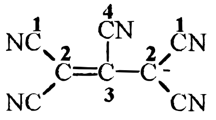
**Table 1. $^1H$ and $^{13}C$ NMR Chemical Shifts of the Various Cyanocarbon Anions in DMSO-$d_6$ Solution**



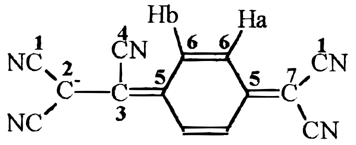
(TCE)



(TCQ)



(PCP)



(PCQ)

| | TCE | PCP | TCQ | PCQ |
|---|---|---|---|---|
| $C_1$ | 114.1<br>115.4<br>117.1 | 113.3<br>116.3 | 118.1 | 115.8<br>119.1 |
| $C_2$ | 54.1 | 57.1 | 43 | 49.3 |
| $C_3$ | 158.2 | 135.8 | 122.5 | 152.4 |
| $C_4$ | | 114.0 | 121.3 | 115.2 |
| $C_5$ | | | 131.4 | 119.8<br>131.6 |
| $C_6$ | | | 153.2 | 119.1<br>130.8 |
| $C_7$ | | | 162 | 68 |
| $C_8$ | | | 114.6 | |
| Hb | | | 6.2<br>6.2 | 6.9<br>7.0 |
| Ha | | | 7.0<br>7.6 | 7.7<br>7.8 |

**Table 2. Polymerization of the Various Monomers in a Homogeneous DMF Solution (60 °C/16 h)**

| monomer | [M]/mol·L$^{-1}$ | $10^3$[AIBN]/mol·L$^{-1}$ | yield/% | $10^{-5}M_w$[a] |
|---|---|---|---|---|
| M-TCE | 0.8 | 8.1 | 79 | 2.25 |
| M-PCP | 1.0 | 5.5 | 97 | 5.30 |
| M-TCQ | 1.0 | 5.0 | 44 | *b* |
| M-PCQ | 1.0 | 5.0 | 0 | |
| | 1.0 | 10.0 | 0 | |
| | 1.0 | 20.0 | 0 | |
| M-TPB | 1.0 | 5.5 | 78 | 6.43 |
| VI-PCP | 1.0 | 5.0 | 22 | 0.21 |
| VI-PCQ | 1.0 | 10.0 | 0 | |

[a] Light-scattering measurements (see Experimental Section). [b] Too strong absorption of the polymer solution for reliable light-scattering measurements.

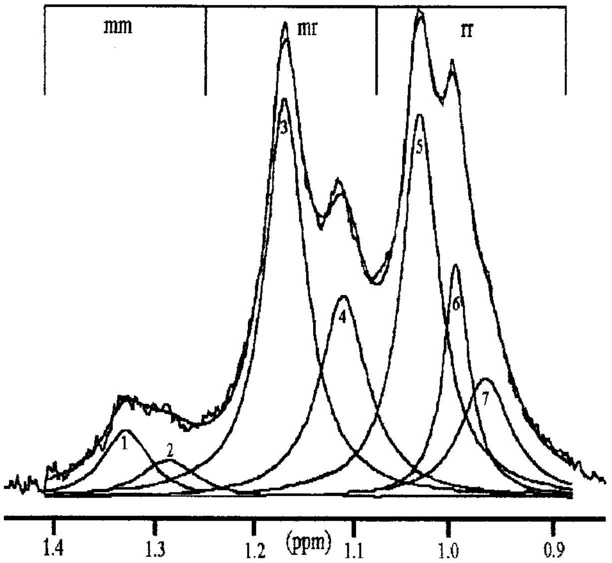


**Figure 1.** $^1H$ NMR spectrum of the α-$CH_3$ backbone group of P(M-PCP) (DMSO-$d_6$, 120 °C): (1 and 2) mmmr + mmmm + rmmr; (3) rmrr + mmrm; (4) rmrm + mmrr; (5) rrrr; (6) mrrr; (7) mrrm.

**Table 3. Tacticities[a] of the Polyelectrolyte P(M-PCP) and the Two Homologous Electrolyte P(M-Cl) and Zwitterionic P(M-Z) Methacrylate Chains Obtained at 60 °C**

| polymers | (mm) | (mr) | (rr) | *P*(m/r) | *P*(r/m) | *P*(m) |
|---|---|---|---|---|---|---|
| P(M-PCP) | 0.087 | 0.450 | 0.463 | 0.327 | 0.727 | 0.312 |
| P(M-Cl) | 0.075 | 0.420 | 0.505 | 0.294 | 0.737 | 0.285 |
| P(M-Z) | 0.110 | 0.414 | 0.476 | 0.303 | 0.649 | 0.315 |

[a] $P(m/r) = 1 - P(r/r) = (mr)/[2(rr) + mr]$ for first-order Markov statistics and $P(m) = 1 - P(r) = (mm) + (mr)/2$ for Bernoulli statistics if $P(m/r) + P(r/m) = 1$.

An alternative strategy toward the target polymers with PCQ counterions relies on ion exchange between the polyelectrolyte precursors P(VI-I) or P(M-Cl) and the tetramethylammonium salt of the cyanocarbon acid ($PCQ^-,N^+(CH_3)_4$). Thus, homogeneous DMF solutions of stoichiometric mixtures of the polymers and the salt were directly precipited into water. The recovered water-insoluble polymers show a nearly quantitative degree of ion exchange of about 90% and 97% for P(VI-I) and P(M-Cl), respectively (see Experimental Section).

The monomer panel should be easily broadened by chemical variations either on the organophilic anion or on the polymerizable cation. In the first case, other monovalent and still more delocalized cyanocarbon anions,[19] such as 1,1,2,3,4,5,5-heptacyanopentadienide for instance, are good candidates but with the drawback of a typical UV spectrum incompatible with light-scattering measurements ($\epsilon \sim 33\,000$ L·mol·cm$^{-1}$ at $\lambda = 528$ nm for the given example), as for the previous TCQ and PCQ anions. The colorless tetraphenylboride anion (TPB) was briefly considered in the methacrylic series as a possible alternative. The monomer synthesis (see Experimental Section) and its radical polymerization (see Table 2) are straightforward, but the corresponding high-molecular-weight polymer actually displays less interesting solubility properties (insolubility in formamide, for instance). In the second case, very usual precursor cationic monomers of technological importance such as (4-vinylbenzyl)trimethylammonium chloride or diallyldimethylammonium chloride (cyclopolymerization) are likely excellent candidates. On the contrary, because of its high sensitivity toward anionic polymerization even in the presence of weak bases, 4-vinylpyridinium triflate[33] risks being an hazardous precursor despite its definite interest.

**Solubility Properties.** They were essentially studied on the polymer P(M-PCP) of high molecular weight ($M_w \sim 5.3 \times 10^5$). As expected from its chemical structure, it is water-insoluble over the whole temperature range (0−100 °C) but readily dissolved in a very broad range of organic solvents at room temperature. These solubility properties are better discussed considering separately aprotic and protic solvents.

(a) Efficient aprotic solvents are essentially defined by the presence in their structure of a dipolar bond as outlined below.

C═O: ketones, lactones, cyclic carbonates, linear or cyclic tertiary amides, 2-alkyloxazolidinones, fully substituted linear or cyclic ureas.

S═O and O═S═O: linear and cyclic sulfoxides and sulfones, tertiary sulfonamides.

P═O: phosphates, phosphoramides, phosphonates, phosphonamides.

$NO_2$, C≡N: nitro and cyano aliphatic and aromatic compounds.

The best solvents are found in the first members of these series, which cover a broad range of cohesive energy density (Hildebrand solubility parameter $\delta_H \sim$ 20−30 MPa$^{1/2}$) and of dielectric permittivity ($\epsilon \sim$ 10−90). As a most characteristic common feature, they show a dipole moment $\mu$ systematically higher than a critical value of about 2.6 D. In a first approach, this may be considered as a necessary but nonsufficient condition: compare, for instance, the solubility of P(M-PCP) in triethyl phosphate (TEP, $\mu = 3.12$ D) with its insolubility in tributyl phosphate (TBP, $\mu = 3.07$ D) of increased steric crowding. In any way, dipole−dipole interactions in the less dissociating solvents (ion pairs strongly predominant over free ions) and ion−dipole interactions in the more dissociating solvents are the major driving forces of the solvation process of the ionic species. However because of the strongly delocalized structure of the anion, polarization interactions may also afford a significant contribution.

(b) Efficient protic solvents are essentially restricted to linear primary and secondary amides such as formamide, *N*-methylformamide, and *N*-methylacetamide (30 °C), which are strongly dipolar and dissociating self-associated solvents ($\delta_H > 28$ MPa$^{1/2}$, $\mu > 3.2$ D, $\epsilon > 100$), and to *m*-cresol, where the rather low polarity ($\mu = 1.48$ D, $\epsilon$(25 °C) = 12.4) is likely balanced by the high polarizability of its aromatic structure. Strong organic acids, such as trifluoroacetic acid or methanesulfonic acid, actually dissolve the polymer. In the last solvent, the UV spectrum [$\lambda_{nm}$ ($\epsilon$ in L·mol$^{-1}$·cm$^{-1}$): 412 (12 700), 430 (13 500)] shows a significant bathochromic shift and a simultaneous hypochromicity with respect to that observed in acetonitrile solution [$\lambda_{nm}$ ($\epsilon$ in L·mol$^{-1}$·cm$^{-1}$): 396 (21 900), 415 (20 300). It is difficult to ascribe such a spectrum change only to pure solvatochromic effects, and a contribution of partial protonation of the anion cannot be a priori ruled out. However, the UV spectrum of the model salt, tetramethylammonium 1,1,2,3,3-pentacyanopropenide, is barely modified when going from pure aqueous solution to 85% sulfuric acid,[34] and this anion has been thus assumed to resist protonation even in such a highly acidic medium.

Aliphatic or aromatic hydrocarbons and their halide derivatives, alcohols, ethers, and carboxylic acids and their esters and amines are all nonsolvents of the polyelectrolyte.

The overall solubility properties are likely finely tuned by two independent contributions: solvation of the neutral polymethacrylate main chain and solvation of the ionic species (see above). For a given solvent these two contributions may be additive or opposite, and in the latter case, solubility obviously depends on their relative importance. For instance, P(M-PCP) is highly soluble in acetonitrile, which is a very good solvent of the model salt but a very poor solvent of poly(methyl methacrylate) (PMMA) ($\theta$ temperature 28 °C, more collapsed conformation than that in the other $\theta$ solvents[35]). However within this simplified approach, ether−alcohols, such as 2-methoxyethanol or tetrahydrofurfuryl alcohol, and fluorinated alcohols, which are all good solvents of PMMA and of the model low-molecular-weight salt, should also be good solvents of the polyelectrolyte: this is not the case, as shown by the rather low maximum solubility of about 1 g·dL$^{-1}$ observed at room temperature in these media. The solubility properties are clearly more complex.

**Viscosity of the Polyelectrolyte in Salt-Free Organic Solutions.** All the viscosity measurements were performed at 25 °C on the unfractionated polymer P(M-PCP) ($M_w \sim 5.3 \times 10^5$) mostly in the concentration range 0.015−1 g·dL$^{-1}$ in a series of solvents covering a very broad range of dielectric constants, from $\epsilon$(25 °C) = 10.79 for triethyl phosphate (TEP) to $\epsilon$(25 °C) = 182.4 for *N*-methylformamide (NMF).

Besides the usual excluded volume effects, the viscosity behavior of polyelectrolytes essentially reflects the electrostatic interactions arising from the chain dissociation into a macroion and free counterions. This process is monitored by the solvent nature at two successive levels: (a) through the intrinsic dissociation of an ion pair $K_d$, as observed for low-molecular-weight electrolytes, which is a strongly increasing function of the solvent dielectric constant [For instance, according to literature data,[36] tetramethylammonium 1,1,2,3,3-pentacyanopropenide (PCP−TMA$^+$) shows a dissociation constant $K_d$ of $4.6 \times 10^{-4}$ L·mol$^{-1}$ in the binary mixture acetone−carbon tetrachloride of dielectric constant $\epsilon$(25 °C) = 10.3 while it is almost quantitatively dissociated in acetonitrile, $\epsilon$(25 °C) = 35.94.] and (b) through the Manning condensation,[37] typical of the very high functionality of the chain structure, which limits in any way the fraction of free counterions to an upper value *f* given by

$$f = b/l_B \quad \text{when} \quad b < l_B \tag{2}$$

$$l_B = e^2/(4\pi\epsilon\epsilon_0 k_B T) \tag{3}$$

where *b* is the distance between two vicinal ionic sites along the chain (*b* = 2.56 Å for a methacrylic backbone) and $l_B$ is the Bjerrum length, which is the distance overwhich electrostatic interactions between two charges (*e*) in a medium of dielectric constant $\epsilon$ become lower than the thermal energy $k_BT$ ($k_B$, Boltzmann constant).

The dissociation extent is actually monitored by the Manning condensation except for solvents where $\alpha < b/l_B$, where $\alpha$ is the dissociation degree derived in a first

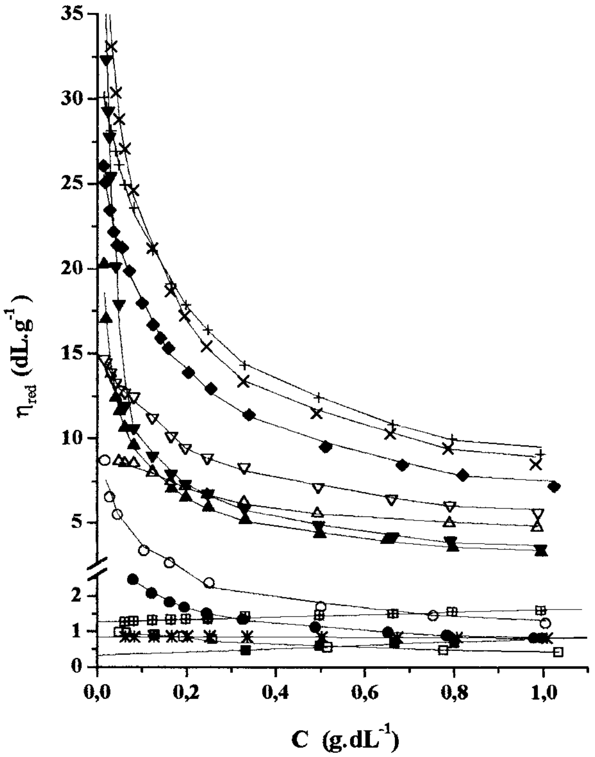


**Figure 2.** Concentration dependence of the reduced viscosities of P(M-PCP) in various solvents at 25 °C: (■) TEP; (□) CP; (●) CH; (○) AC; (▲) ACN); (△) DMF; (▼) NA; (▽) DMSO; (◆) PC; (+) EC−PC; (×) CPY; (*) F; (⊞) MF.

**Table 4. Viscosity (25 °C) and Light-Scattering Measurements (Room Temperature) on Polyelectrolyte P(M-PCP) in Dilute Solution in Various Solvents: Triethylphosphate (TEP), Formamide (F), *N*-Methylformamide (MF), and Dimethylformamide (DMF)**

| solvent | $[\eta]$/ dL·g$^{-1}$ | $K_H$ | d$n$/d$c^a$/ mL·g$^{-1}$ | $10^{-5}M_w$ | $10^{-3}A_2$/ mL·g$^{-2}$·mol | $(S_Z{}^2)^{0.5}$/Å |
|---|---|---|---|---|---|---|
| TEP | 0.376 | 4.5 | 0.172 | 4.00 | 3.46 | 250 |
| F | 0.86 | −0.05 | 0.138 | 1.25 | 5.16 | 550 |
| MF | 1.27 | 0.21 | 0.157 | 0.744 | 6.68 | 350 |
| MF$^b$ | 1.19 | 0.23 | | | | |
| DMF$^c$ | | | 0.155 | 5.30 | 0.275 | 420 |

[a] d$n$/d$c$ values poorly obey the Gladstone's relation d$n$/d$c$ (mL·g$^{-1}$) = (1.265−0.777)$n_D$, $R(4) = -0.976$. [b] Measurements performed at 40 °C. [c] In the presence of $(CH_3)_4N^+$,PCP$^-$ at a concentration of 0.05 mol·L$^{-1}$.

approach from the dissociation constant $K_D$ of an isolated ion pair at the same concentration. Since α and $l_B$ respectively increase (in a complex way) and decrease when increasing the dielectric constant of the solvent $\epsilon$, it is not possible to express the previous critical conditions as a simple function of $\epsilon$. However, using $K_D$ in the literature[36] for the model salt PCP$^-$TMA$^+$ in a series of solvents of $\epsilon < 21$ (quantitative dissociation for higher $\epsilon$ values), it may be calculated that, in the concentration range involved in the viscosity measurements ($3 \times 10^{-4}$ mol·L$^{-1}$ < $c \leq 3 \times 10^{-2}$ mol·L$^{-1}$), α always remains higher than $b/l_B$. Thus, for all the systems under study, ionic dissociation should be essentially limited by the Manning condensation. When going from the least to the most dissociating medium, TEP and NMF, respectively, $l_B$ decreases from 51.9 to 3.1 Å and, conversely, $f$ increases from 0.05 to 0.83. The solvent range actually allows us to consider most of the possible situations, from very low to very high dissociation extents, much higher than that observed in aqueous solution ($f = 0.36$).

The variations of the reduced viscosities $\eta_{red}$ with concentration are given in Figure 2. Three main behaviors may be clearly identified, and they will be discussed successively.

(a) *In triethyl phosphate solution* where ionic dissociation, if any, is minimum and very weak (see above), the linear variations $\eta_{red} = f(c)$ merely show that the polyelectrolyte behaves as a neutral chain. The extrapolated intrinsic viscosity of 0.27 dL·g$^{-1}$ is lower than that of an homologous polyelectrolyte in aqueous salt solution[13] (same polycation of identical degree of polymerization, DP$_w$ = 1550, neutralized by benzenesulfonate counterions: $[\eta] = 0.40$ dL·g$^{-1}$ in 0.5 M KCl), and the Huggins coefficient $K_H = 4.5$ is unusually high: these features may suggest some intramolecular clustering of the ion pairs. Light-scattering measurements in salt-free solution performed in a lower concentration range ($c \sim 0.1-0.02$ g·dL$^{-1}$) lead to a classical Zimm plot (at least for scattering angles ≥ 30°) and to the apparent values given in Table 4. The $M_w$ value, only 25% lower than the true one, may be discussed according to the simplified expression of the scattered intensity at zero scattering vector $q$ for salt-free polyelectrolyte solution:[38]

$$(KC/I)q = 0 = (1/M_w)(1 + Z/k + 2A^2M_wc) \qquad (4)$$

where $Z$ is the total effective charge per polymer chain and $k$ is a factor which depends on the contributions of the various charged species to the electrostatic screening: $k = 1$ if only the counterions are taken into account. Within this assumption, the calculated $Z$ value is very low, $Z = 0.33$. Not much physical meaning should however be ascribed to this value, because of the oversimplifications involved in its derivation, but the small difference between the apparent and the true $M_w$ values is consistent with the lack of polyelectrolyte behavior observed in viscosity experiments. Finally, for comparison, it may be of interest to estimate the dissociation degree α of the model salt under identical conditions of molar concentration and dielectric constant of the solvent using literature data[36] (see above): when the salt concentration increases from $3 \times 10^{-4}$ to $3 \times 10^{-3}$ and $3 \times 10^{-2}$ mol·L$^{-1}$ (corresponding to the polymer concentrations 0.01, 0.1, and 1 g·dL$^{-1}$), α decreases from 0.69 to 0.32 and 0.12.

(b) *For the second series of solvents of medium to high dielectric constants in the range 13 (cyclopentanone)−90 (2-cyanopyridine)*, a typical polyelectrolyte behavior is actually observed, characterized by a strong $\eta_{red}$ increase when decreasing the concentration. Moreover in most cases, the higher the dielectric constant of the solvent, the higher the absolute values of $\eta_{red}$: at a constant and low enough concentration of 0.1 g·dL$^{-1}$, they are a linearly increasing function of the solvent dielectric constant, but this fact lacks any theoretical grounds and may be purely incidental. All these features are obviously consistent with a significant ionic dissociation and with a maximum fraction of effective charges per chain increasing from 0.06 to 0.42 when going from the least dissociating cyclopentanone (CP, $\epsilon$(25 °C) = 13.58) to the most dissociating 2-cyanopyridine (CPy, $\epsilon$(30 °C) = 89.7) medium. The viscosimetric behavior may be interpreted through semiempirical equations which generally involve some $c^{-0.5}$ dependence of the reduced viscosities to take into account the

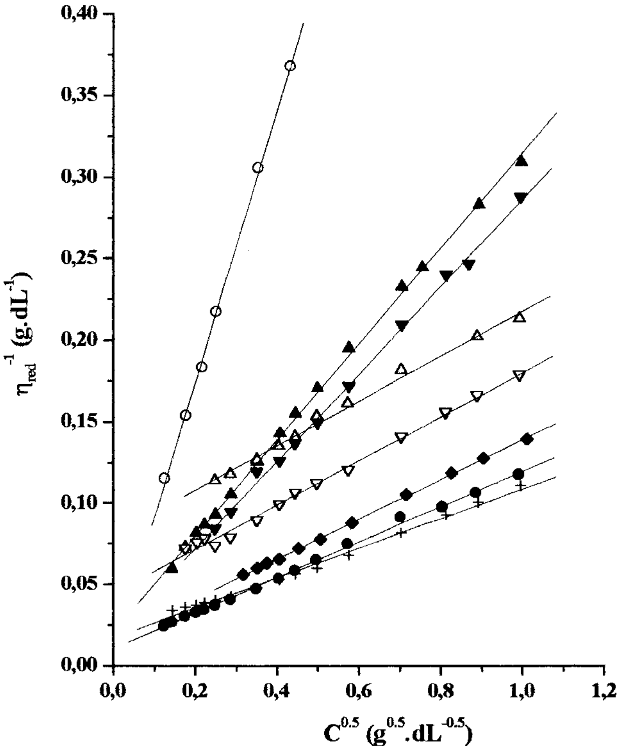


**Figure 3.** Fuoss plot (eq 5) of the viscosimetric data of P(M-PCP) in the various solvents at 25 °C (same symbols as in Figure 2).

screening of electrostatic interactions by the polymer itself in salt-free solution. All the experimental data may be linearized over a broad enough concentration range (0.06 g·dL$^{-1}$ < $c$ < 1 g·dL$^{-1}$) according to the most famous Fuoss equation:[39]

$$\eta_{\text{red}} = A/(1 + BC^{0.5}) + D \tag{5}$$

The term $D$ is typically negligible, so eq 5 is most often written in a simplified form with only two coefficients.[3,4,6,7] The corresponding plots are given in Figure 3. According to various theoretical calculations, for a polyelectrolyte of a given molecular weight, the ratio $A/B$ of the Fuoss parameters directly reflects the number of effective charges per chain $Z$.

$$\text{Witten−Pincus approach}^{40} \qquad A/B \propto Z^2 \tag{6}$$

$$\text{Rabin approach}^{41} \qquad A/B \propto Z \tag{7}$$

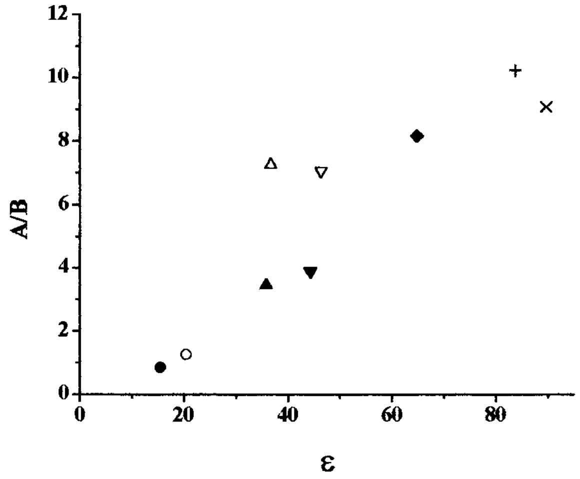


**Figure 4.** Variations of the ratio $A/B$ of the Fuoss parameters with the dielectric constant of the solvents (same symbols as in Figure 2).

Viscosity measurements on a series of polystyrene ionomers of low sodium sulfonate content (<10 mol %) better agree with Rabin's predictions.[42] The variations of the $A/B$ experimental values with the dielectric constant of the solvent are given in Figure 4. As expected, the general trend is actually an increase of the $A/B$ ratio when increasing the dissociation power of the medium, but without any reliable correlation. It may be stressed that the previous relations (eqs 6 and 7) have been severely criticized because of the strong oversimplifications and of the crudeness of the models involved in their derivation.[6] Moreover, the significant difference between acetonitrile and dimethylformamide of nearly identical dielectric constant is of special interest. The decrease by a factor of 2 of the characteristic $A/B$ ratio in acetonitrile likely results from a more collapsed chain conformation in this very poor solvent of the polymer backbone (see Solubility Properties), which induces an enhanced counterion condensation (eq 2 is restricted to a rodlike conformation). Thus, the lack of a strong correlation between $A/B$ and $\epsilon$ may merely reflect that, even in solvents of fairly high dissociation power, the thermodynamic affinity of the medium for the main chain actually contributes to the overall behavior of the system through the usual excluded volume effects. According to recent studies on stoichiometric polyelectrolyte−surfactant complexes in a series of organic solvents and in water for the polyelectrolyte precursor ($\epsilon \sim 18-78$), the charge density $Z$ is a weakly linear increasing function of the medium dielectric constant ($Z \sim (6.2 + 0.1)\epsilon$) and remains unexpectedly quite low:[18] $Z \sim 7-14$ for a chain bearing about 4500 ionogenic sites (DP$_n$ ~ 4500). The $A/B$ values measured for our systems are compatible with these results.

As an alternative to the Fuoss equation, the Yan−Dougherty−Stivala equation[43] has recently been used in the case of an analogous system, Nafion 117 in a series of organic solvents[15] ($\epsilon \sim 17-78$):

$$\eta_{\text{red}} = [\eta]_\infty + k[\eta]_\infty c^{-0.5} \tag{8}$$

Our experimental data also obey eq 8, which does not however provide any additional information ($[\eta]_\infty \equiv A$).

Finally, it is of interest to notice that weak but significant dissociation effects are already observed in cyclohexanone while they cannot be detected for polystyrene ionomers (molar fraction of sodium sulfonate ≤ 0.04) in the same solvent.[44] Besides the overall ionic content, the nature of the ion pair is likely a factor of the observed difference. The very strong symmetric delocalization of the negative charge over the planar PCP ion should be favorable to higher dissociation.[36]

(c) *For the two solvents of the highest dielectric constants, formamide (F,* $\epsilon$(25 °C) = 108.0) and *N*-methylformamide (NMF, $\epsilon$(25 °C) = 182.4), the variations $\eta_{\text{red}} = f(c)$ are linear over the concentration range 0.06−1.0 g·dL$^{-1}$ (Figure 2). This behavior is a priori unexpected and puzzling, since these two solvents should lead to maximum fractions of dissociated ion pairs, $f$ = 0.49 and 0.83, respectively. Light-scattering measurements, performed in a partly common concentration range ($c \sim 0.02-0.3$ g·dL$^{-1}$, usual Zimm plots) lead to apparent $M_w$ values much lower than the true one, as shown in Table 4, and to corresponding $Z$ values derived through eq 4 of 3.3 and 6.1 in formamide and *N*-methylformamide, respectively. The use of eq 4 is much more hazardous than in the first case of TEP solution, and these light-scattering data have no quantitative physical meaning. However they suggest that ionic dissociation is likely stronger than that in TEP solution but still too weak to be identified through viscosity measurements in these solvents. A tentative analysis of this viscosity behavior relies on the fact that primary and secondary amide type solvents are nonsolvents for the polymethacrylic main chain at room temperature. For instance, poly(methyl methacrylate) is insoluble in formamide, and the cloud points corresponding to upper critical solution temperatures for a sample of $M_w \sim 5 \times 10^5$ at a concentration of 1 g·dL$^{-1}$ are about 77 and 91 °C in *N*-methylformamide and *N*-methylacetamide, respectively. The binary systems P(M-PCP)/F or MF are thus typical of polyelectrolytes dissolved in poor solvents, which have already received much attention at the theoretical level, at least for chains of low charge density.[7,45−47] In the absence of charges, the chain would be in a strongly collapsed conformation which results for a polyelectrolyte in a quasi-quantitative counterion condensation ("cascade" condensation[45]). The chain swelling in the presence of charges from a globular conformation to "a string of poor solvent blobs" would occur only if the electrostatic energy is sufficient to overcome the interfacial energy which must be paid when more chain segments are exposed to the poor solvent.[7] However, this transition may likely be induced by a very small effective charge density on the chain. The systems under investigation may correspond to such a limited but significant swelling: the extrapolated intrinsic viscosities given in Table 4 are much higher than that calculated for a dense spherical particle impenetrable to the solvent (Einstein model, $[\eta] = 2.5 \times$ specific volume $\sim 0.025$ dL·g$^{-1}$) and still higher than that observed in a good but non dissociating solvent such as triethyl phosphate or that calculated for the homologous random coil in aqueous salt solution ($[\eta] = 0.40$ g·dL$^{-1}$, see above). The tentative model of a polyelectrolyte in a poor solvent may be further tested through a short analysis of the temperature influence on the behavior of the P(M-PCP)/MF system. As clearly shown in Figure 5, a temperature increase up to 40 °C does not change the polymer behavior, but a further increase up to 50 and then to 60 °C results in a progressive enhancement of the $\eta_{red}$ values and in the simultaneous development of weak polyelectrolyte effects, as evidenced by the upturn of the variations $\eta_{red}$ versus $c$ at low concentration. The solvent dielectric permittivity decreases only from 181.5 at 25 °C to 148.8 at 50 °C, and the typical change of the viscosimetric behavior may be thus essentially ascribed to a transition from a very poor to a better solvent for the polyelectrolyte main chain: stronger excluded volume effects allow higher ionic dissociation and the emergence of a polyelectrolyte behavior, despite the weak decrease of the dielectric constant. Assuming in a very crude model that the electrostatic and the usual excluded volume effects are of the same order of magnitude and merely additive, the variations $\eta_{red} = f(c)$ may be analyzed in a first approach through a modified form of the Huggins equation according to[18]

$$\eta_{red} = [\eta] + k_H[\eta]^2 c + kc^{-0.5} \tag{9}$$

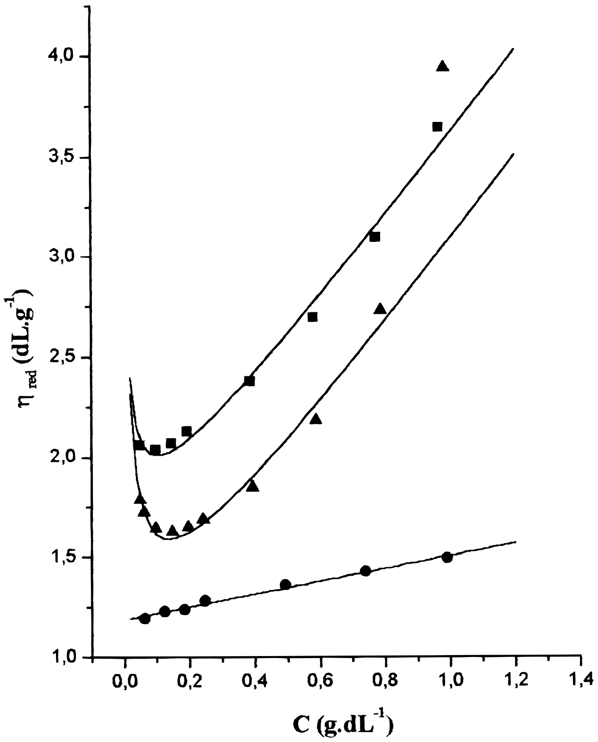


**Figure 5.** Concentration dependence of the reduced viscosities of P(M-CP) in *N*-methylformamide as a function of temperature: (●) 40 °C; (▲) 50 °C; (■) 60 °C. The curved lines at 50 and 60 °C are calculated according to eq 9.

The experimental data actually obey eq 9, as shown in Figure 5 (determination of the curve parameters by linear multiple regression analysis), and this good agreement may be considered as an argument in favor of the model.

Finally, comparison with the scarce literature data related to polyelectrolytes in the same type of solvents remains ambiguous. For Nafion 117[15] (see Introduction), the lack of any polyelectrolyte effects and the low extrapolated $[\eta]$ values may be reasonably interpreted along the same lines, since formamide and *N*-methylformamide likely show very poor affinity for this perfluorinated copolymer. However for statistical acrylamide sodium acrylate copolymers[14] (molar fraction of ionic units $\sim$ 0.15−0.70) the lack of any polyelectrolyte effects in pure formamide or in water−formamide mixtures (water volume fraction < 0.5) cannot be taken into account in the same way, since water and formamide are both good solvents of polyacrylamide.

## Conclusion

Among the cationic quaternary ammonium polyelectrolytes associated with strongly delocalized cyanocarbon anions, poly[(2-methacryloyloxy)ethyl]trimethylammonium 1,1,2,3,3-pentacyanopropenide] may be considered as a most representative and scarce example of an hydrophobic polyelectrolyte of high charge density showing an unusual spectrum of solubility in dipolar solvents ($\mu > 2.6$ D) covering a very broad range of dielectric constants ($\epsilon \sim 10-180$). Its homogeneous chemical structure avoids the amphiphilic character of the polysoaps[16,17] or of the stoichiometric surfactant−polyelectrolyte complexes:[18] it may thus appear as an optimized and very versatile model for the separation and the quantitative analysis of the usual excluded volume effects and of the specific electrostatic interactions which monitor all the static and dynamic solution properties of polyelectrolytes. As clearly shown by the previous experimental results, systematic variations of the solvent and of the temperature allow us to consider the same polyelectrolyte in all the possible situations of ionic dissociation and of thermodynamic affinity of the solvent for the main chain and to consider the corresponding transitions between all these different regimes. It is thus the hope of the authors that future studies on these systems may afford at the experimental level a significant contribution to the complex and fascinating field of statistical physics of polyelectrolyte solutions. Last but not least, some intrinsic properties of the cyanocarbon moieties, such as fluorescence for the PCP anion,[48] must not be ignored and could provide some additional interest to these new hydrophobic polyelectrolytes.

## Experimental Section

**Solvents, Reagents, Cyanocarbon Salts, and Monomers.** All the solvents and reagents of the best reagent grade available were used without further purification.Tetracyanoethylene oxide (TCNEO),[49] tetramethylammonium 1,2,2-tricyanoethenolate,[21,22] 1,1,2,3,3-pentacyanopropenide[21–23] *p*-(tricyanovinyl)phenyldicyanomethide,[25] and sodium α,α′-dicyano-*p*-toluoylcyanide[24] were all prepared according to the literature (Caution! hydrogen cyanide is evolved in some syntheses). [2-(Methacryloyloxy)ethyl]trimethylammonium chloride (M-Cl) was used as a 75 wt % aqueous solution (Atochem). 3-Methyl-1-vinylimidazolium iodide (VI-I) was obtained by quaternization of 1-vinylimidazole with methyl iodide according to an optimization of a literature process[20] (acetonitrile instead of tetrahydrofuran as solvent) with a yield of 98%.

**[(2-Methacryloyloxy)ethyl]trimethylammonium 1,2,2-Tricyanoethenolate (M-TCE).** TCNEO (11.53 g, 0.08 mol) was slowly added to a solution of 9.52 g of KBr (0.08 mol) in 60 mL of water, and stirring was continued until complete dissolution. To this dark-red solution was added dropwise 22.4 g of the aqueous M-Cl solution (0.08 mol), and the mixture was left overnight at 5 °C to lead to 17.4 g of the crude yellowish product (yield of 75%). Recrystallization from ethanol solution (23 mL·g$^{-1}$) gave the pure tan salt with an overall yield of 62%. $T_m = 82.5-82.8$ °C. $^1$H NMR (DMSO-$d_6$) δ (ppm) 6.07 and 5.75 (2H, $CH_2$=), 4.51 (2H, $OCH_2$), 3.70 (2H, $N^+CH_2$), 3.12 (12H, $N^+(CH_3)_4$), 1.89 (3H, $CH_3C$=). UV (ACN) $\lambda_{nm}$ ($\epsilon$ in L·mol$^{-1}$·cm$^{-1}$): 297 (10540). Anal. Calcd for $C_{14}H_{18}N_4O_3$: C, 57.92; H, 6.25; N, 19.30; O, 16.33. Found: C, 57.96; H, 6.24; N, 19.33; O, 16.57.

**[(2-Methacryloyloxy)ethyl]trimethylammonium 1,1,2,3,3-Pentacyanopropenide (M-PCP).** To a solution of 25.02 g (0.2 mol) of TCNE in 180 mL of acetone precooled to −50 °C was added dropwise under stirring a mixture of 16.10 mL (0.2 mol) of pyridine in 18 mL of water and 20 mL of acetone. The solution was stirred until the temperature reached 20 °C, and 55.4 g of the aqueous M-Cl solution (0.2 mol) were then added dropwise. After removal of acetone by rotary evaporation at room temperature, precipitation of the residual solution into 1.6 L of water gave 30.4 g of the crude yellow product (yield of 90%). Recrystallization from aqueous ethanol (13 mL of ethanol + 9.8 mL of water per gram of of salt) lead to 25.4 g of bright-yellow crystals with an overall yield of 75%. $T_m = 108.2-108.5$ °C. $^1$H NMR: see M-TCE. UV (ACN) $\lambda_{nm}$ ($\epsilon$ in L·mol$^{-1}$·cm$^{-1}$): 396 (22 600), 414 (22 000). Anal. Calcd for $C_{17}H_{18}N_6O_2$: C, 60.34; H, 5.36; N, 24.84; O, 9.46. Found: C, 60.33; H, 5.30; N, 24.87; O, 9.51.

**[(2-Methacryloyloxy)ethyl]trimethylammonium α,α-Dicyano-*p*-toluoylcyanide (M-TCQ).** To a solution of 3.5 g (0.016 mL) of sodium α,α-dicyano-*p*-toluoylcyanide in a mixture of 250 mL of acetone and 25 mL of water was added 4.46 g (0.016 mol) of the aqueous M-Cl solution. After removal of acetone by rotary evaporation, the residual dark-red aqueous suspension was exhaustively extracted with methylene chloride. The organic solution was concentrated by rotary evaporation and crystallization at −15 °C after addition of a small amount of hexane lead to 3.3 g of dark-red crystals (yield of 56%). $T_m = 85.0-85.7$ °C. $^1$H NMR (DMSO-$d_6$) δ (ppm): see M-TCE for M and 6.76−6.86 (2H, Ar), 7.51−7.65 (2H, Ar). UV (ACN) $\lambda_{nm}$ ($\epsilon$ in L·mol$^{-1}$·cm$^{-1}$): 281 (6110), 330 (1040), 480 (41 550). Anal. Calcd for $C_{20}H_{22}N_4O_3$: C, 65.56; H, 6.05; N, 15.29; O, 13.10. Found: C, 65.28; H, 6.05; N, 15.19; O, 13.26.

**[(2-Methacryloyloxy)ethyl]trimethylammonium *p*-(tricyanovinyl)phenyldicyanomethide. (M-PCQ).** A solution of 12 g (0.06 mol) of TCNQ and of 6 g (0.09 mol) of malononitrile in 200 mL of DMF was stirred at 75 °C for 45 min. The dark-blue mixture was poured into 2 L of ice-cooled water, and 126.3 g of the aqueous M-Cl solution (0.46 mol) was then added under stirring, giving 24 g (yield of 96%) of the crude product as a dark-blue precipitate. Recrystallization from a mixture of 600 mL of ethanol and 190 mL of acetonitrile lead to dark-blue crystals with an overall yield of 92%. $T_m = 149-150$ °C. $^1$H NMR (DMSO-$d_6$) δ (ppm): see M-TCE for M and 6.90−6.95 (2H, Ar), 7.73−7.78 (2H, Ar). UV (ACN) $\lambda_{nm}$ ($\epsilon$ in L·mol$^{-1}$·cm$^{-1}$): 643 (52 000). Anal. Calcd for $C_{23}H_{22}N_6O_2$: C, 66.65; H, 5.35; N, 20.28; O, 7.72. Found: C, 66.82; H, 5.36; N, 20.32; O, 7.86.

**[(2-Methacryloyloxy)ethyl]trimethylammonium Tetraphenylboride (M-TPB).** To a solution of 6.84 g (0.02 mol) of sodium tetraphenylboride in 10 mL of water was added dropwise 5.54 g of the aqueous M-Cl solution (0.02 mol) under stirring. The white precipitate was recovered by filtration, thoroughly washed with water, and dried under vacuum. Yield: 91%. $T_m = 159$ °C. $^1$H NMR (DMSO-$d_6$) δ (ppm): see M-TCE for M and 7.16 (4 × 1H, Ar), 6.88 (4 × 2H, Ar), 6.80 (4 × 2H, Ar). UV (ACN) $\lambda_{nm}$ ($\epsilon$ in L·mol$^{-1}$·cm$^{-1}$): 266 (3350), 274 (2180). Anal. Calcd for $C_{33}H_{38}NO_2B$: C, 80.65; H, 7.79; N, 2.85. Found: C, 80.58; H, 7.77; N, 2.74.

**Tetramethylammonium tetraphenylboride** was made via transposition of the experimental procedure for the synthesis of M-TPB, starting from tetramethylammonium chloride. Yield: 96%. $T_m > 300$ °C. $^1$H NMR (DMSO-$d_6$) δ (ppm): see M-TPB for TPB and 3.06 (12H, $N^+(CH_3)_4$). UV (ACN) $\lambda_{nm}$ ($\epsilon$ in L·mol$^{-1}$·cm$^{-1}$): 266 (3730), 274 (2480). Anal. Calcd for $C_{28}H_{32}NB$: C, 85.49; H, 8.20; N, 3.56. Found: C, 85.10; H, 8.14; N, 3.39.

**1-Vinyl-3-methylimidazolium 1,1,2,3,3-pentacyanopropenide (VI-PCP)** was made via transposition of the experimental procedure for the synthesis of M-PCP, starting from VI-I. Recrystallization of the crude product (yield of 90%) from aqueous acetone (4.5 mL of acetone + 3.5 mL of water per gram of product) lead to bright-yellow crystals with an overall yield of 80%. $T_m = 112-112.5$ °C. $^1$H NMR (DMSO-$d_6$) δ (ppm): 5.4 and 5.9 (2H, $CH_2$=), 7.25 (1H, =CHN), 9.40 (1H, NCH=$N^+$), 7.80 (1H, NCH=$CHN^+$), 8.10 (1H, NCH=$CHN^+$), 3.87 (3H, $CH_3$). UV (ACN) $\lambda_{nm}$ ($\epsilon$ in L·mol$^{-1}$·cm$^{-1}$): 396 (22 660), 414 (22 080). Anal. Calcd for $C_{14}H_9N_7$: C, 61.08; H, 3.29; N, 35.62. Found: C, 61.07; H, 3.20; N, 35.66.

**1-Vinyl-3-methylimidazolium *p*-(tricyanovinyl)phenyldicyanomethide (VI-PCQ)** was made via transposition of the experimental procedure for the synthesis of M-PCQ starting from VI-I. Recrystallization of the crude product (yield of 88%) from a binary mixture of acetonitrile−diethyl ether (2 mL ACN + 4.5 mL $Et_2O$ per gram of product) lead to dark-blue crystals with an overall yield of 77%. $T_m = 121.1-122.7$ °C. $^1$H NMR: see VI-TCE for VI and M-PCQ for PCQ. UV (ACN) $\lambda_{nm}$ ($\epsilon$ in L·mol$^{-1}$·cm$^{-1}$): 643 (50 840). Anal. Calcd for $C_{20}H_{13}N_7$: C, 68.37; H, 3.73; N, 27.90. Found: C, 68.43; H, 3.66; N, 27.80.

**Polymers.** All polymerizations were carried out in a Pyrex glass double-walled reactor fitted with a magnetic stirrer and connected with an external Lauda thermostat, allowing the temperature to be monitored within ±0.1 °C. The system containing the solvent, monomer, and initiator (previously recrystallized azobis(isobutyronitrile), AIBN, or azobis(cyanovaleric acid), ACVA) was degassed at room temperature by three successive vacuum−argon sweeping cycles and the polymerization was thus performed at constant temperature and for a given time (see text) under a slight pressure of argon.

**Poly{[(2-methacryloyloxy)ethyl]trimethylammonium chloride} P(M-Cl).** Polymerization of M-Cl was performed in homogeneous aqueous solution under the following experimental conditions: [MCl] = 0.5 mol·L$^{-1}$, [ACVA] = 3.63 × 10$^{-3}$ mol·L$^{-1}$, $T$ = 60 °C, time $t$ = 15 h. The viscous solution was diluted with water and then exhaustively dialyzed against distilled water using Spectrapor membranes (molecular weight cutoff 3500) to remove the residual monomer and finally freeze-dried to afford the polymer with a yield of 62%. Its average molecular weight was $M_w = 1.33 \times 10^6$ (d$n$/d$c$ = 0.160 mL·g$^{-1}$ in $H_2O$−0.1 M NaCl).

**Poly(1-vinyl-3-methylimidazolium iodide) P(VI-I)** was made via transposition of the experimental procedure for P(M-Cl): [VI-I] = 1 mol·L$^{-1}$, [ACVA] = 5 × 10$^{-3}$ mol·L$^{-1}$, $T$ = 60 °C, time $t$ = 16 h. Yield: 60%. $M_w = 4.34 \times 10^5$ (d$n$/d$c$ = 0.163 mL·g$^{-1}$ in $H_2O$−0.1 M $(CH_4)_4N^+I^-$.

**Hydrophobic Polyelectrolytes.** After polymerization (see detailed experimental conditions in Table 2), the homogeneous solution of the polymer in DMF was diluted with acetone if too viscous and then precipitated into a large excess of methanol. The polymer was recovered by filtration, thoroughly washed with methanol, and finally dried at 50 °C under vacuum. In some cases, residual monomer, if detected on the $^1$H NMR spectrum, was exhaustively removed by Soxhlet extraction with methanol. For the M and VI-PCQ polymerization, the precipitation did not occur in methanol but in diethyl ether, resulting in the quasi-quantitative recovery of the initial monomer identified through its $^1$H NMR spectrum.

**Synthesis of Poly[1-vinyl-3-methylimidazolium *p*-(tricyanovinyl)phenyldicyanomethide] P(VI-PCQ) from P(VI-I) by Ion Exchange.** A solution of 0.474 g (1.5 mmol) of $(CH3)_4N^+PCQ^-$ in 5 mL of DMF was slowly added under stirring to a solution of 0.358 g (1.5 mmol) of P(VI-I) in 15 mL of DMF. The homogeneous mixture was stirred further for 2 h and then precipitated in 300 mL of water: the insoluble polymer was recovered by filtration, thoroughy washed until the aqueous filtrate became colorless, and dried under vacuum. Yield: 77% with respect to the quantitatively exchanged polymer. Anal. Calcd for P(VI-0.9 PCP-0.1 I)·0.31$H_2O$: C, 74.58; H, 3.86; N, 26.31; O, 1.46; I, 3.79. Found: C, 64.61; H, 3.87; N, 26.89; O, 1.46; I, 3.77.

**Synthesis of Poly{[(2-methacryloyloxy)ethyl]trimethylammonium *p*-(tricyanovinyl)phenyldicyanomethide} P(M-PCQ) from P(M-Cl) by Ion Exchange.** Transposition of the experimental procedure for P(VI-PCQ). Yield: 77%. Anal. Calcd for P(M-0.97 PCP-0.03 Cl)·0.20$H_2O$: C, 65.85; H, 5.32; N, 19.90; O, 8.54; Cl, 0.26. Found: C, 65.45; H, 5.48; N, 20.25; O, 8.54; Cl, 0.27.

**Spectroscopy Measurements.** IR (KBr pellets) and UV spectra (ACN solution) were recorded on a Perkin-Elmer 983 and a Shimadzu UV-2101 PC spectrometer, respectively. $^1$H and $^{13}$C NMR measurements were performed in DMSO-$d_6$ solution on a Brucker AC 200 spectrometer at room temperature except for tacticity analysis, which was carried out at 120 °C. For $^1$H NMR spectra, the chemical shifts $\delta$ are given in ppm with respect to the solvent resonance fixed at 2.49 ppm.

**Light Scattering Measurements.** Specific index increments (d$n$/d$c$, mL g$^{-1}$) were measured at room temperature on a Brice−Phenix BP 1000V differential refractometer fitted with a neon laser beam ($\lambda$ = 632 nm). Light-scattering measurements were performed at room temperature on a Sematech 633 apparatus at the same wavelength. For molecular weight determination on the various polyelectrolytes, experiments were carried out in DMF solutions in the presence of the corresponding tetramethylammonium homoanionic salt at a concentration of 0.05 mol·L$^{-1}$ using the following measured d$n$/d$c$ values: 0.094, 0.155, 0.170, and 0.196 mL·g$^{-1}$ for P(M-TCE), P(M-PCP), P(M-TPB), and P(VI-PCP), respectively.

**Viscosity Measurements.** They were carried out on a Sematech automatic device of the Ubbelohde type and restricted to concentrations leading to a viscosity difference between the solution and the solvent of at least 10%. For experiments performed in *N*-methylformamide at high temperature, the actual concentrations were calculated assuming identical thermal expansion coefficients for the solutions and the solvent:[52] $\alpha = 8.69 \times 10^{-4}$ K$^{-1}$. Whenever possible, the intrinsic viscosity [$\eta$] was calculated from the classical Huggins equation: $\eta_{red} = [\eta] + k_H[\eta]^2c$, where $k_H$ is the Huggins constant.

**Identification and Physical Characteristics of the Solvents.** The values of the dipole moment ($\mu$, D), of the dielectric constant ($\epsilon$), and of the Hildebrand solubility parameter ($\delta_H$, MPa$^{0.5}$) of the various solvents were taken from literature compilations.[50,51] For the binary mixtures, the $\epsilon$ value was calculated assuming a simple additivity rule based on volume fractions. The solvent identification (dielectric constant at 25 °C given within parentheses) is as follows: triethyl phosphate, TEP (10.79); cyclopentanone, CP (13.58); cyclohexanone, CH (15.61); acetone, AC (20.56); acetonitrile, ACN (35.94); dimethylformamide, DMF (36.71); 2-nitroanisole, NA (44.32); dimethyl sulfoxide, DMSO (46.45); propylene carbonate, PC (64.92); ethylene carbonate−propylene carbonate, EC−PC (7:3 by vol, 86.2); 2-cyanopyridine−pyridine, CNP (95% by vol, 89.72 at 30 °C); formamide, F (108.03); *N*-methylformamide, MF (182.4).

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