Poly(ammonium alkoxydicyanoethenolates) as New Hydrophobic and Highly Dipolar Poly(zwitterions). 1. Synthesis

Marie-Laure Pujol-Fortin and Jean-Claude Galin*

Institut Charles Sadron (CRM-EAHP) (CNRS-ULP) 6, Rue Boussingault, 67083 Strasbourg Cedex, France

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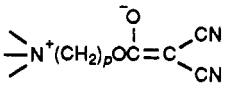
ABSTRACT: The nucleophilic ring opening of dicyanoketene ethylene (p = 2) or propylene (p = 3) acetals by tertiary amino monomers readily leads to new crystalline zwitterionic species characterized by the dipolar structure



Sixteen monomers were obtained with yields over 70% in the aliphatic (acrylates and methacrylates) or in the heterocyclic (vinylpyridine, *N*-vinylimidazole) series. Their free-radical polymerization in homogeneous solution in dipolar aprotic solvents (DMF, DMSO) initiated by azobisisobutyronitrile at 60 °C is straightforward. In the methacrylate series, molecular weight may be easily controlled from 5×10^6 to 1×10^5 by using 2-mercaptoethanol as a transfer agent (C_T = 0.14). The zwitterionic moiety has been characterized by spectrometry (IR, UV, and ^{13}C NMR) and by the UV analysis of its protonation in concentrated H_2SO_4 or $HClO_4$ solutions:

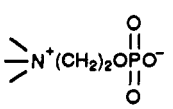
$$>N^+A^- + H^+ \underset{K_a}{\rightleftharpoons} >N^+AH$$

$pK_a \simeq -3.7$ according to the Boyd cyanocarbon acidity scale.

Introduction

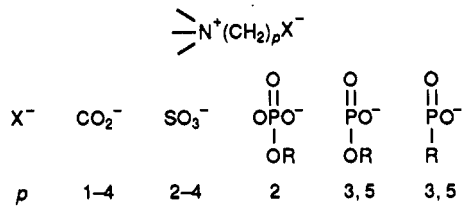
Since their emergence more than 30 years ago,[1,2] and after a rather long period of relative oversight, stable zwitterionic polymers have recently received increased attention. The very high dipole moment of their functionalized unit imparts to these macromolecular chains a series of specific and unique properties, e.g.: (a) "antipolyelectrolyte" behavior in water solution[3-8] as typified by an increasing chain expansion when the ionic strength of the medium is increased; (b) strong intermolecular association in nonpolar solvents or in bulk for telechelic chains[9,10] or statistical copolymers;[11] (c) chelating properties toward transition-metal salts[12] and the ability to dissolve in bulk mineral salts of widely different lattice energies (NaCl, $LiClO_4$) up to stoichiometric amounts yielding amorphous blends;[13] (d) microphase separation in statistical copolymers arising from zwitterion clustering in the apolar matrix,[14-18] similar to that found in the well-known ionomers.

Moreover, natural phospholipids are amphiphilic systems where the polar hydrophilic head is an ammonium phosphobetaine



and their outstanding biological importance has promoted an ever increasing amount of studies on analogous zwitterionic polymeric monolayers and liposomes as synthetic models for biomembranes.[19,20]

The more stable zwitterionic structures generally belong to the quaternary ammonium betaines where the anionic site may be a carboxylate,[1,11,12,21] a sulfonate,[2,18,22,23] a phosphate,[19,20] a phosphonate, or a phosphinate group:[12]



In the course of our work, we became interested in the development of new zwitterionic structures essentially characterized by a stronger delocalization of the negative charge over the organic moiety. The expected increase in polarizability and decrease in hydrophilicity could result in significantly improved properties for the corresponding polymers with respect to solubility in organic media, specific interactions with polar species, and stability of bulk properties. Some zwitterionic structures already reported in the polymer literature meet at least partly these requirements, but with some unavoidable drawbacks:

(a) In chemically stable sulfonium[24-27] or ammonium[28-30] ylides, the dipole moment is obviously relatively low since the opposite charges are located in vicinal sites (compare, for instance, μ = 9.3 D for pyridinium dicyanomethylide[31] versus μ = 25 D for triethylammonium (sulfopropyl)betaine[32]) and moreover some structures display unfavorably high photosensitivity.[28,29]

(b) The zwitterionic form in the much studied spirobenzopyran merocyanine dyes is stable only in well-defined conditions of microenvironment polarity, light irradiation, temperature, or state of aggregation[33-36] of the dye.

As early as 1958, Middleton et al.[37] discovered that the nucleophilic ring opening of cyclic dicyanoketene acetals

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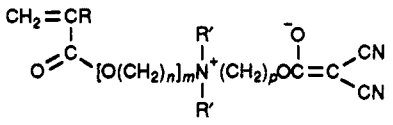
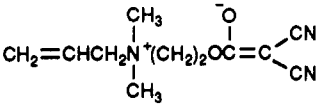
Chart I

acrylic and methacrylic



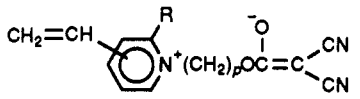
R	R′	n	m	p = 2	p = 3
H	CH_3	2	1	**1a**	**1b**
CH_3	CH_3	2	1	**2a**	**2b**
CH_3	CH_3	3	1	**3a**	**3b**
CH_3	C_2H_5	2	2		**4b**

allylic

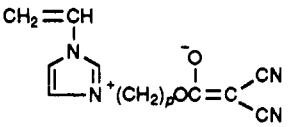


5a

heterocyclic

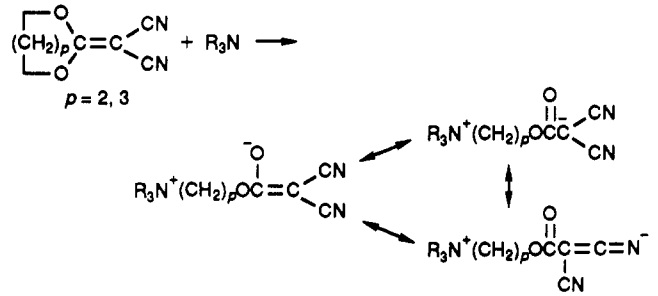


R	vinyl position	p = 2	p = 3
H	2	**6a**	**6b**
H	4	**7a**	**7b**
CH_3	5	**8a**	**8b**



9a; 9b

by tertiary amines readily leads to new zwitterionic species, 2,2-dicyano-1-(2-trialkylammonioalkoxy)ethenolates, where their cyanocarbon anionic moiety is characterized by a very strong charge delocalization and a very weak basicity:



Transposition of such a synthetic scheme to macromolecular chemistry appears quite promising, and the purpose of this article is to present the synthesis of new aliphatic or heterocyclic zwitterionic monomers of the ammonium dicyanoethenolate type and a survey of their free-radical polymerization leading to hydrophobic poly(zwitterions) that are soluble in dipolar aprotic solvents.

Results and Discussion

Synthesis and Characterization of the Zwitterionic Monomers. The ring opening of the cyclic dicyanoethylene or propylene acetals (DCKEA and DCKPA, respectively) by tertiary amino monomers was carried out at room temperature in acetone or tetrahydrofuran (THF) solution using a stoichiometric concentration of the reagents. The aliphatic or heterocyclic zwitterionic monomers synthesized are detailed in Chart I. Every monomer is noted by a figure for the precursor amino species and a letter **a** or **b** for the structure derived from ethylene and propylene cyclic acetals, respectively.

In most cases, the reaction proceeds with high yields over 70% and appears more rapid and efficient with DCKEA than with DCKPA. The lower yield observed with 2-vinylpyridine (only 59 and 40% for **6a** and **6b** in 3 days) probably arises from steric hindrance at the nitrogen nucleophilic site as observed for analogous quaternization of heterocycles by tetracyanoethylene oxide for instance.[38] No reaction may be observed with *N*-vinylcarbazole. Dialkyl sulfides are also known to yield analogous sulfonium zwitterions, but with drastically reduced rates due to their lower nucleophilicity.[37] In our experiments, ethylthiomethylmethacrylate leads in 2 weeks to a poor yield of 24% of a partially polymerized mixture of the zwitterionic species and the original monomer containing ~20% unreacted sulfide.

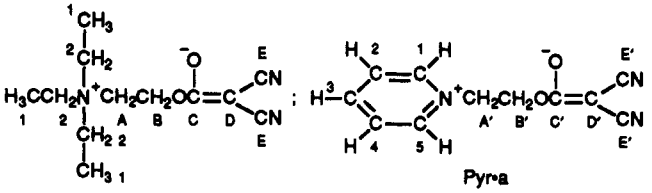
Generally the monomers crystallize out of the reaction medium in a pure enough form for most polymerization experiments (see Experimental Section). Heating of the monomers through their melting points (systematically higher for the heterocyclic compounds and characterized by enthalpies in the range 100–200 $J \cdot g^{-1}$ as compared with 145 $J \cdot g^{-1}$ for the model $Et_3N \cdot$**a**) is immediately followed by polymerization except for the *N*-vinylimidazole zwitterion, which appears stable in the liquid state up to 200 °C. Structural characterization of the monomers was carried out by IR and NMR spectrometry and acid–base potentiometry using the corresponding triethylammonium or pyridinium zwitterions as reference model compounds. They show strong specific IR absorptions:[37] (a) a sharp doublet at 2189 and 2162 cm^{-1}, characteristic of the vibration $\nu(C{\equiv}N)$ of the cyano groups with a high degree of ionic character, as for instance in salts of acylmalononitrile[39] or in pyridinium dicyanomethylide,[40] $C_5H_5N^+C^-(CN)_2$. It systematically occurs in all monomers, with a slight shift to 2198 and 2170 cm^{-1}; (b) a broad absorption at 1652 cm^{-1}, characteristic of the C=C double bond in mesomeric equilibrium with a carbonyl function $OC(O)^-C$. It cannot be identified unambiguously in the various monomers where the unsaturation of the acrylic polymerizable double bonds or of the heterocyclic moieties affords strong and broad absorption in the same frequency range, 1660 ± 10 cm^{-1}.

The ^1H NMR and ^{13}C NMR spectra of the zwitterionic model compounds are detailed in Table I. The most characteristic feature is probably the two clearly separated resonance peaks of the nonequivalent cyano groups.

The anionic site of the zwitterion is a weak base, as clearly shown by the very low pK_a of the conjugated acid of the model $Et_3N \cdot$**a**, measured in strongly concentrated H_2SO_4 or $HClO_4$ aqueous solution, $pK_a = -3.70$ (see further). However, its accurate and quantitative titration may be readily achieved with CF_3SO_3H in CH_3CO_2H as titrating reagent and a mixture of acetic anhydride–acetic acid (9:1 by volume) as solvent; this system was already used successfully for ammonium sulfopropylbetaines.[41] All the zwitterionic species under study afford 1 ± 0.02 basic equiv/mol.

Finally, at room temperature, all these crystalline monomers are insoluble in water but highly soluble either in strongly dipolar aprotic solvents (μ > 3.5 D) such as dimethylformamide (DMF), dimethylacetamide (DMAC), *N*-methylpyrrolidone (NMP), and dimethyl sulfoxide (DMSO) or in protic solvents with strong hydrogen bond donating power, such as fluorinated alcohols, e.g., trifluoroethanol (TFE) and hexafluoro-2-propanol (HFIP). Ether alcohols such as furfurylic or tetrahydrofurfurylic alcohol are poor though definitely better solvents than methanol or ethanol.

Table I
^1H and ^{13}C NMR Characteristics of the Model Zwitterions



Et_3N·a

Pyr·a

	Et_3N·a						
	1	2	A	B	C	D	E
^1H NMR, δ ppm	1.16 t	3.28 m	3.44 t	4.27 m			
^{13}C NMR, δ ppm	8.15						122.10
	7.98	53.93	56.08	56.31	169.36	31.85	121.65
	7.81	53.75					

	Pyr·a							
	1, 5	2, 4	3	A′	B′	C′	D′	E′
^1H NMR, δ ppm	9.00 d	8.15 t	8.62 t	4.57 t	4.83 t			
^{13}C NMR, δ ppm	145.86	127.77						121.30
	145.83	127.68	145.23	60.24	60.69	168.47	30.93	120.88

Table II
Free-Radical Polymerization of the Zwitterionic Monomers at 60 °C

monomer	[M], mol·L^{-1}	[AIBN], mol·L^{-1} × 10^3	solvent	time, h	yield, %	dn/dc, mL·g^{-1}	$\bar{M}_w$ × 10^{-5}
1.a	0.80	4.0	DMSO	4.25	97	0.107[a]	1.09
1.b	0.80	4.0	DMF	3.30	82	0.106[a]	1.10
2.a-1	0.80	4.0	DMSO	2.50	86	0.118[a]	33.80
2.a-2	0.80	4.1	DMAC	2.00	84	0.118[a]	9.25
2.b	0.80	4.0	DMSO	1.00	59	0.070[b]	48.30
3.a	0.15_5	3.9	DMF	19.50	77	0.106[b]	1.35
3.b	0.15_5	4.0	DMF	22.50	65	0.102[a]	1.13
5.a-1	1.50	7.6	DMSO	41.00	0[e]		
5.a-2	1.50	7.4[c]	DMSO[d]	115.00	0[e]		
5.a-3	4.95	25.3[c]	H_2O[d]	48.00	0[e]		
6.a	0.80	4.3	DMSO	28.50	55	0.156[a]	0.54
7.a	0.80	3.9	DMSO	6.70	58	0.171[a]	4.89
8.a	0.80	4.0	DMSO	29.00	32		
9.a	0.80	4.0	DMSO	6.00	51	0.098[b]	2.92

[a] In DMF. [b] In DMSO. [c] With azobis-2-methylpropionamidine dihydrochloride as initiator. [d] Polymerization at 50 °C. [e] Freeze-drying of the solution after reaction allows quantitative recovery of the unpolymerized monomer.

Overview of the Free-Radical Polymerization of the Zwitterionic Monomers. Polymerization was carried out in DMF or DMSO solution at 60 °C in the presence of AIBN as radical initiator.

The representative results given in Table II may suggest the following comments:

(a) In all cases, polymerization proceeds in homogeneous solution. In DMAC as solvent, however, phase separation occurs for conversion higher than ~50% (see run **2a**-2); the solvation power of DMAC for the poly(zwitterion) will be discussed in terms of LCST behavior in a further publication.

(b) As expected for an identical polymerizable double bond, the small variation of zwitterionic structure between monomers **a** and **b** (two and three methylene groups between the charged sites, respectively) has no significant effect on the monomer reactivity (see runs **1a** and **1b** in Table II).

(c) For identical polymerization conditions, the methacrylic monomers (run **2a**-1) lead to the highest degrees of polymerization ($\overline{DP}_w$ higher than 10^4 may be easily obtained), while the 2-vinylpyridine zwitterion yields only very short chains (run **6a**, $\overline{DP}_w$ = 200). This behavior is similar to that previously observed with the corresponding ammonium sulfopropylbetaine monomers[41] and may be tentatively related to enhanced steric hindrance in the 2-vinylpyridinium monomer and the corresponding growing macroradical. It may be stressed that the chain rigidity of this polymer as observed in light scattering experiments (anisotropic behavior, characterized by a rather high Cabannes factor of ~0.31 for $\overline{DP}_w$ = 220) is in good agreement with the assumed steric effects. As expected, the average degree of polymerization in the methacrylic series may be readily monitored by using convenient transfer agents. 2-Mercaptoethanol–monomer **2a** in DMF at 60 °C was chosen as a representative system: [**2a**] = 0.3 M, [AIBN] = 1×10^{-3} M, $0.07 < [HS(CH_2)_2OH]\ 10^3\ M < 4.5$. The transfer constant of the thiol, C_T, was derived from the variations of the weight-average degree of polymerization $\overline{DP}_w$ of the recovered polymers (conversion restricted to less than 20%) with the transfer agent concentration [TA], accordingly to the modified Mayo equation ($\overline{DP}_w$ instead of $\overline{DP}_n$):[42]

$$A_w/\overline{DP}_w = 1/\overline{DP}_w^0 + C_T[TA]/[M]$$

with $A_{w,D} = 2$ for termination exclusively by disproportionation and $A_{w,C+D} = 1 + [1 + 3\,\overline{DP}_w/\overline{DP}_w^0]^{0.5}$ in the other cases. The experimental results, linearized in Figure 1, lead to C_T values of 0.14 (disproportionation only) and of 0.28, significantly lower than that obtained for methyl methacrylate polymerized at the same temperature either in bulk, C_T = 0.62,[43] or in benzene solution, C_T = 0.45.[44]

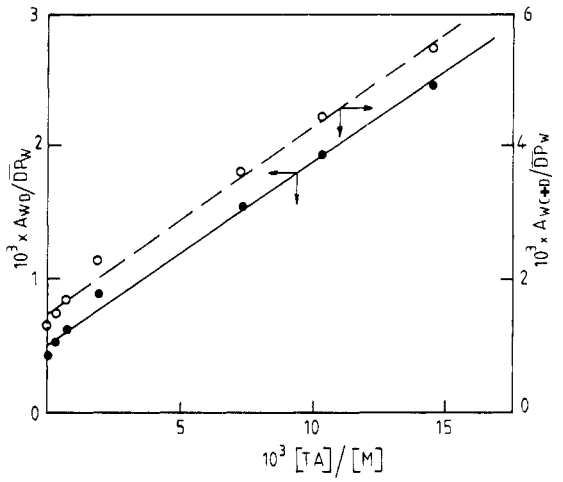


Figure 1. Calculation of the transfer constant of 2-mercaptoethanol in the polymerization of monomer **2a** according to the modified Mayo equation. Termination by disproportionation (●) and by disproportionation + combination (○).

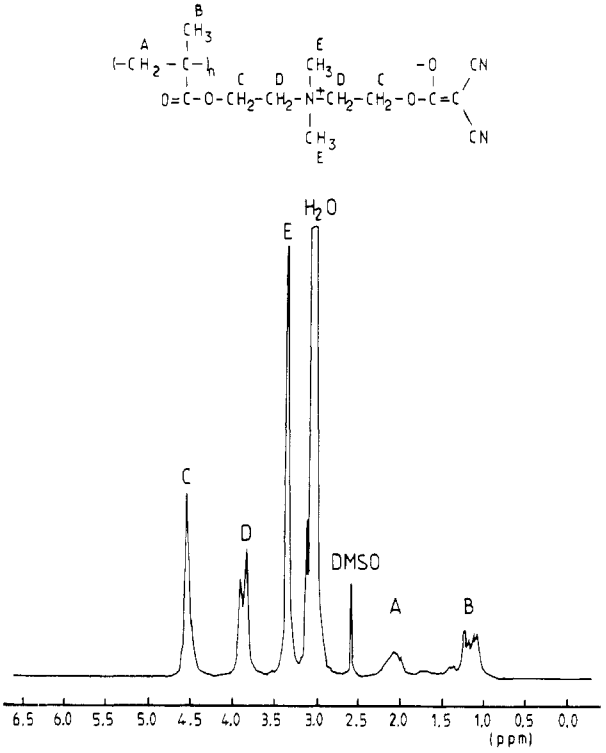
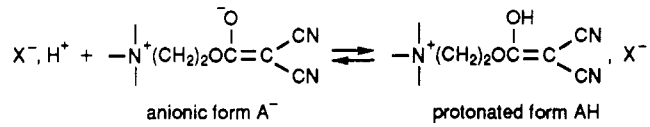


Figure 2. ^{1}H NMR spectrum of **P2a** in DMSO-d_6 at 100 °C.

(d) The allylammonium zwitterion **5a** fails to polymerize in a variety of experimental conditions (runs **5a**-1, **5a**-2, and **5a**-3) and more especially in saturated aqueous solution at 50 °C ([monomer] = 4.9 M) in the presence of azobis-2-methylpropionamidine dihydrochloride (run **5a**-3); dimethylallylammonium chloride, however, readily yields chains of significant degrees of polymerization ($\overline{DP}$ = 90–480) in similar conditions except for a higher monomer concentration (7 M).[45] The origin of such different behavior still remains obscure.

Spectrometric Characterization of the Poly(zwitterions). All the characteristic spectrometric features (ν(C≡N) absorption in IR and ^{1}H and ^{13}C NMR resonances) of the zwitterionic moiety are obviously preserved when going from the monomers to the polymers, and the ^{1}H NMR spectrum of **P2a** is given in Figure 2 as a representative example. Chain tacticity, and its dependence on temperature and solvent nature, will be discussed in the forthcoming communication. The UV measurements on the zwitterionic poly(acrylates and methacrylates) and on their model compound (Et_3N·**a**) were performed in TFE solution (where unfortunately the other polymers are insoluble). The spectra show two characteristic absorption bands at about 201 and 238 nm. The longer wavelength better defined band is characteristic of the delocalized anionic moiety, as explained further. Beer's law is well obeyed within the range 3×10^{-4}–2×10^{-3} mol·L^{-1}, leading to the absorptions given in Table III. The zwitterionic absorption shows a very slight hypsochromic shift and a weak but significant hypochromicity when going from the model to the polymers.

Acid–Base Equilibria in Concentrated H_2SO_4 and $HClO_4$ Aqueous Solutions. In contrast with their insolubility in water or in weak acids such as acetic acid, the low molecular weight model compound Et_3N·**a** and the poly(zwitterion) **P2a** are soluble in concentrated aqueous solutions of strong acids such as H_2SO_4 or $HClO_4$ (≃38–60% by weight). The progressive decrease of the characteristic absorption band of the cyanocarbon anion at λ = 238–240 nm when the acid concentration is increased is very similar to that previously observed under the same conditions by Boyd[46] on sodium methyldicyanoacetate of identical structure, reflecting the protonation of the anionic site according to the following acid–base equilibrium:



The acid form does not contribute significantly to the absorption at λ = 238–240 nm, and UV spectroscopy thus allows in principle direct monitoring of the variation of the ratio $R = [A^-]/[AH]$ with the acid concentration. Unfortunately, as for sodium methyldicyanoacetate,[46] strongly acidic solutions of the zwitterions are not stable toward hydrolysis and annealing at room temperature for a few hours leads first to a slow decrease of the absorption band with a progressive red shift up to 251 nm and, for longer times (>4 h), to the appearance of a new band at 300–310 nm.

In the same way, the IR spectrum of the polymer previously swollen in 93.8% H_2SO_4 shows a very drastic decrease of the cyano doublet at 2170–2190 cm^{-1} and a new sharp absorption at 2328 cm^{-1}, in the range of triple or cumulated double bonds, which we were unable to identify. As expected for an unimolecular degradation process, the irreversible reaction monitored by UV spectroscopy (model and polymer concentrations in the range 1–1.5 $\times 10^{-3}$ mol·L^{-1}) obeys first-order kinetics with a low enough rate constant k to allow reliable extrapolation of the experimental data to zero time (see Figure 3). Degradation is slower in $HClO_4$ (k (h^{-1}) ~ $5 \times 10^{-3} - 1 \times 10^{-2}$) than in H_2SO_4 (k (h^{-1}) ~ 2×10^{-2}–5×10^{-2}), but no definite trends may be derived for the influence of acid concentration or from the comparison between the model and the polymer. The acidity constant of the protonated form of the zwitterion may be determined by using the H-acidity function developed by Boyd for a series of homologous cyanocarbon acids:[47]

$$H_- = pK_a + \log [A^-]/[AH] \quad (1)$$

where [A$^-$] and [AH] are the equilibrium concentrations of the base and its conjugated acid. In our case, for every H_2SO_4 and $HClO_4$ solution, the ratio $R = [A^-]/[AH]$ may be derived from UV data according to $R = \epsilon/(\epsilon_{TFE} - \epsilon)$

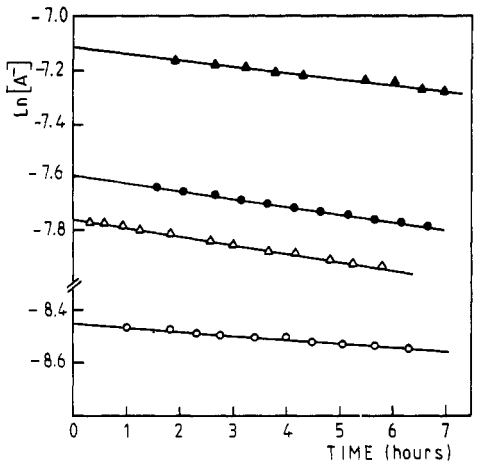


Figure 3. First-order kinetics of the decay of the anionic site for the zwitterionic model Et_3N·a and for the polymer P2a in various acidic solvents. H_2SO_4(56%)–Et_3N·a (○); H_2SO_4(56%)–P2a (●); H_2SO_4 (51%)–Et_3N·a (△); H_2SO_4 (51%)–P2a (▲).

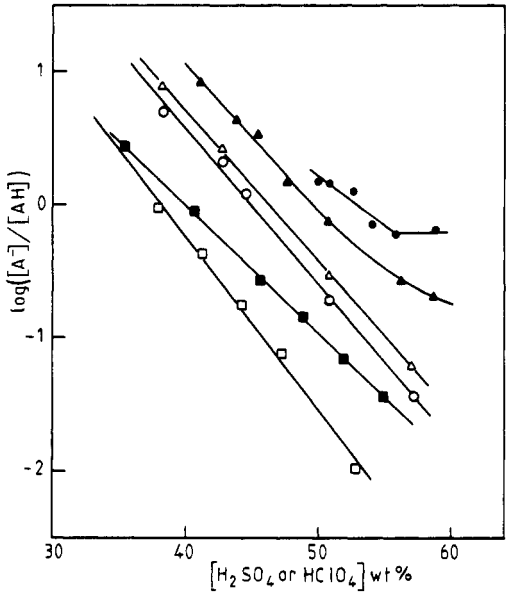


Figure 4. Variation of the protonation degree of the model Et_3N·a and the polymeric P2a zwitterions in various acidic solutions. H_2SO_4–P2a (●); H_2SO_4–Et_3N·a (▲); H_2SO_4–sodium methyldicyanoacetate (■); $HClO_4$–P2a (○); $HClO_4$–Et_3N·a (△); $HClO_4$–sodium methyldicyanoacetate (□).

Table III
UV Transitions of the Model and of the Acrylic and Methacrylic Poly(zwitterions) in Trifluoroethanol at Room Temperature

	Et_3N·a	P1a	P2a	P3a
λ_{max}, nm	238	236	236	236
ϵ, L·mol^{-1}·cm^{-1}	18 200	16 950	15 600	15 300
λ_{max}, nm	200	202	202	202
ϵ, L·mol^{-1}·cm^{-1}	13 750	12 700	12 800	11 550

where ϵ is the zwitterionic molar absorptivity extrapolated to zero time and ϵ_{TFE} the molar absorptivity of the zwitterion measured in TFE solution where no protonation of the anionic site occurs (solvent effects on the anion UV transition are assumed negligible).

Figure 4 shows the variations of log R versus the acid concentration for all the systems investigated and for sodium methyldicyanoacetate chosen as a reference compound of identical anion structure and of known pK_a value: pK_a = −2.63 and −2.78 in $HClO_4$ and H_2SO_4, respectively.[46,47]

The pK_a values of the protonated zwitterionic species AH may be calculated from eq 1 according to two methods: (a) derivation from the pK_a of the reference compound, provided that the nearly linear variations log R = f(acid concentration) may be superposed by a constant vertical shift over a wide enough acid concentration range.

$$\Delta \log R = \log R_{ref} - \log R \qquad pK_a = pK_{a_{ref}} + \Delta \log R$$

Such a requirement is fairly well fulfilled in all cases but for the poly(zwitterion) in H_2SO_4 solution (see Figure 4); (b) identification of the pK_a values with that of the H acidity function for acid concentration such as R = 1 (the accuracy of the R ratio is maximum at this point).

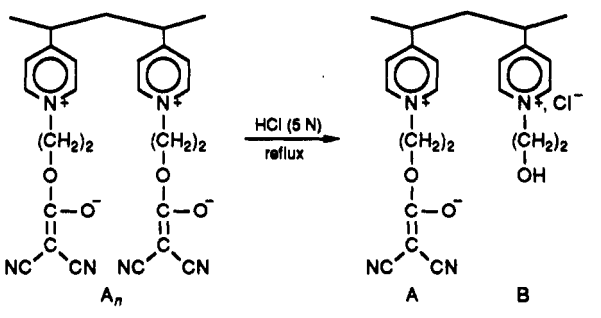
The pK_a values given in Table IV may suggest the following comments:

(a) The acidity strength of all the protonated zwitterionic species is greater by 1 order of magnitude than that of the analogous neutral reference compound; this characteristic feature arises from repulsive Coulombic interactions between the proton and the cationic ammonium site of the zwitterion, which makes the neutralization of its cyanocarbon anion much more difficult.

(b) Comparison of the low molecular weight and of the polymeric zwitterions appears somewhat puzzling since, according to the acid medium, the chain may appear either slightly more (H_2SO_4) or less ($HClO_4$) acidic than its model. Because of cooperative effects of the cationic ammonium sites, the poly(zwitterion) may be reasonably expected less basic than its model, as observed in H_2SO_4 solution, and no satisfactory explanation can be proposed for the reverse behavior observed in $HClO_4$ solution. It may be emphasized, however, that, in this case, the difference is only ~0.16 pK_a unit, quite close to the experimental accuracy. Moreover, the pK_a values for the polymer are obviously apparent values, which do not take into account possible polyelectrolyte effects (continuous variations of the pK_a of the chain when its ionization degree is increased) that cannot be detected from our measurements.

High-Temperature Hydrolysis of the Poly(zwitterion) in Acidic Aqueous Solution. According to the literature,[37] the zwitterions are cleaved in strongly acidic solution at high temperature, leading to quaternary ammonium salts. This process has been transposed to P7a, which does not show any other hydrolyzable bond in its chain.

In the very drastic experimental conditions involved (see reaction scheme and Experimental Section), hydrolysis starts in heterogeneous solution and then proceeds rapidly in a homogeneous way (polymer solubilization by the electrolyte units).



The IR spectrum (complete disappearance of ν(C≡N) at 2196 and 2170 cm^{-1}, broad absorption ν(OH) in the range 3300–3500 cm^{-1}), the elemental analysis data of the recovered samples, and the molecular weight measure-

Table IV
pK_a Values of the Et_3N-a and P2a According to Boyd's Acidity Scale

	38% < ClO_4H < 57%		41% < SO_4H_2 < 58.8%	
	method a	method b	method a	method b
Et_3N-a zwitterionic model	−3.7 ± 0.20	−3.66	−3.75 ± 0.06	−3.75
P2a poly(zwitterion)	−3.55 ± 0.12	−3.48	−4.03 ± 0.06	−4.06

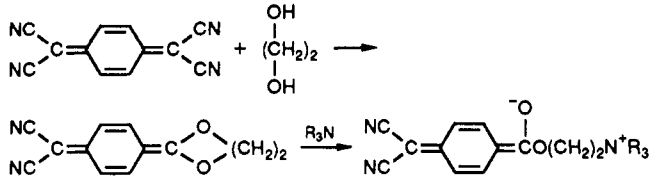
ments (light scattering measurements in TFE–LiCl, 0.1 N) show that the hydrolysis degree increases from 0.64 to 0.93 for reaction times of 0.5 and 5.0 h, respectively, and that chain degradation occurs simultaneously: $\overline{DP}_w$ decreases from its initial value of 2030 to 930 for the shorter reaction time. It would be of interest of check the scission of the hydrocarbon backbone on an analogous poly(4-vinylpyridinium salt) under the same experimental conditions, but this is beyond the scope of the present work.

Solubility Properties in Organic Solvents. The aliphatic poly(zwitterions) under study show solubility properties quite different from those of the poly(sulfopropyl betaines): insolubility in water (even at 100 °C) and even in the presence of a moderate amount of salt (<1 mol·L^{-1}) and solubility in a number of dipolar aprotic solvents such as tertiary amides (DMF, DMAC), sulfoxide (DMSO), and cyclic tetrasubstituted ureas (dimethylethylene or propyleneurea). However, as previously noted, the fluorinated alcohols appear to be good solvents for a variety of zwitterionic chains.

Conclusion

The nucleophilic ring opening of dicyanoketene ethylene (p = 2) or propylene (p = 3) acetals by tertiary amino monomers is a very efficient and versatile route to new stable zwitterionic monomers in both the aliphatic and heterocyclic series. Their free-radical polymerization is straightforward and currently leads to high molecular weight chains. Because of the very peculiar dicyanoethenolate structure of the anionic site of the ammonium betaine lateral groups, these highly dipolar polymers show specific properties quite unusual for poly(zwitterions), such as hydrophobicity and solubility in dipolar aprotic solvents. A detailed analysis of their morphological and hydrodynamical characteristics in dilute solution, with special emphasis on salt effects, will be reported in forthcoming communications.

Finally, even if the synthetic strategy resting upon cyclic dicyanoketene acetals allows some minor variations in the 1,2- or 1,3-diol structure,[37] it would be of outstanding interest to turn to tetracyanoquinodimethane (TCNQ) chemistry in order to get new zwitterions of still higher dipole moments and delocalization of the negative charge, as outlined below:



Hertler et al.[48] described more than 25 years ago the successful condensation of TCNQ with 1,2-diamines or 1,2-diamino alcohols but quite surprisingly without any mention of analogous reactions with 1,2- or 1,3-diols. In our hands, some preliminary attempts fail to yield the desired acetals, and this a priori promising alternative does not appear reliable.

The poly(zwitterions) already synthesized may be considered as excellent polymers meeting most of the requirements detailed in the Introduction, more especially with respect to the high dipole moment of the ammonium betaine function, μ = 26.0 D fo. the model compound.[32]

Experimental Section

Physical Measurements. (a) Melting Point and Potentiometric Measurements. Uncorrected melting points were measured either on a Mettler FP 5 capillary melting point apparatus or on a Perkin-Elmer DSC4 differential calorimeter (heating rate of 1 °C min^{-1}, calibration with indium). Potentiometric measurements were carried out on an automatic Mettler device DK 11 fitted with a joint calomel–glass electrode Metrohm 6.0.203 using a mixture of acetic acid–acetic anhydride (1:9 by volume) as solvent and CF_3SO_3H (0.1 N) in acetic acid as titrating reagent.

(b) Spectrometry. IR (on KBr pellets) and UV spectra were recorded on a Perkin-Elmer 983 and a Cary 2300 spectrometer, respectively. ^1H NMR measurements were performed in DMSO-d_6 solution at 25 °C on a Bruker AC 200 (200 MHz) spectrometer; chemical shifts δ, expressed in ppm, were calculated with respect to the solvent signal fixed at 2.50 ppm. ^{13}C–^1H spectra were recorded on the same spectrometer, operating at 50.3 MHz.

(c) Molecular Weight Measurements. Specific index increments were measured at 25 °C on a Brice-Phoenix BP 1000 V differential refractometer fitted with a neon laser beam (λ = 6320 Å). Light scattering measurements were performed at room temperature on a Fica apparatus for the same wavelength.

Monomer Synthesis and Polymerization. (a) Solvent, Monomer, and Reagent Purification. Solvents were distilled over convenient drying reagents and stored under argon or over molecular sieves (3 or 4 Å) in Schlenk vessels; THF was distilled from disodium benzophenone dianion solutions; DMF, DMSO, DMAC, pyridine (Pyr), and triethylamine (Et_3N) were distilled from CaH_2. The various H_2SO_4 and $HClO_4$ aqueous solutions were prepared by dilution of previously titrated highly concentrated acids (95–97% H_2SO_4, 69—72% $HClO_4$), and their final concentrations were derived from their density in the usual way. The tertiary amino precursor monomers, dimethylallylamine, vinylpyridines, *N*-vinylimidazole, and (dimethylamino)ethylacrylate or -methacrylate were vacuum distilled over CaH_2. (Diethylamino)ethoxyethyl- and (dimethylamino)propylmethacrylates were prepared and purified as previously described.[41] The cyclic dicyanoketene acetals, DCKEA and DCKPA, and the corresponding model zwitterionic compounds derived from triethylamine or pyridine were synthesized and purified according to the literature.[37] The initiator azobisisobutyronitrile (AIBN) and 2,2-azobismethylpropionamidine dihydrochloride (AMPAD) were recrystallized from methanol and acetone–H_2O, respectively. 2-Mercaptoethanol was stored under argon after distillation.

(b) Synthesis of the Zwitterionic Monomers. To a solution of 0.1 mol of DCKEA (or DCKPA) in 50 mL of THF (or acetone) was added dropwise under stirring 0.1 mol of tertiary amino compound (monomer or model), the temperature being kept below 30 °C by external cooling if necessary. The reaction mixture was then stirred at room temperature for 1 and 3 days for the aliphatic and heterocyclic amines, respectively. The generally insoluble zwitterionic monomer was filtered and thoroughly washed with cold acetone. In most cases, the monomer was pure enough as checked by the analytical data given below; it may be further recrystallized if necessary from water or water–methanol mixture (t <60 °C) in the presence of small amounts of hydroquinone with yields in the range 50–90%.

1a: yield 94%; mp 143–144 °C (ΔH = 151 J·g^{-1}); basicity equivalent 0.97; ^1H NMR (DMSO-d_6) δ 6.50–6.15 (m, 3 H, CH_2=CH), 4.60 (m, 4 H, $COOCH_2$ + CH_2OCO^-), 3.90 (m, 4 H, $^+N(CH_2)_2$), 3.38 (s, 6 H, $^+N(CH_3)_2$). Anal. Calcd for $C_{13}H_{17}O_4N_3$: C, 55.90; H, 6.14; O, 22.91; N, 15.05. Found: C, 55.90; H, 6.17; O, 23.09; N, 15.10.

1b: yield 83%; mp 115 °C; basicity equivalent 0.98; ^1H NMR (DMSO-d_6) δ 6.34, 6.26, 6.03 (m, 3 H, CH_2=CH), 4.51 (m, 2 H, $COOCH_2$), 3.94 (t, 2 H, CH_2OCO^-), 3.69 (m, 2 H, N^+CH_2), 3.40 (t, 2 H, N^+CH_2), 3.08 (s, 6 H, $^+N(CH_3)_2$), 1.98 (m, 2 H, $N^+CH_2CH_2$-

CH_2). Anal. Calcd for $C_{14}H_{19}O_4N_3$: C, 57.32; H, 6.53; O, 21.82; N, 14.33. Found: C, 57.33; H, 6.49; O, 21.55; N, 14.27.

2a: yield 93%; mp 136.9–137.4 °C (ΔH = 115 J·g^{-1}); basicity equivalent 1.00; ^{1}H NMR (DMSO-d_6) δ 6.10 and 5.75 (2 s, 2 H, CH_2=CCH_3), 4.50 (m, 2 H, $COOCH_2$), 4.40 (m, 2 H, CH_2OCO^-), 3.80 (t, 2 H, N^+CH_2), 3.70 (t, 2 H, N^+CH_2), 3.17 (s, 6 H, $N^+(CH_3)_2$), 1.91 (s, 3 H, CH_2=CCH_3). Anal. Calcd for $C_{14}H_{19}O_4N_3$: C, 57.33; H, 6.53; O, 21.81; N, 14.33. Found: C, 57.43; H, 6.59; O, 21.69; N, 14.38.

2b: yield 70%; mp 144–145 °C (ΔH = 113 J·g^{-1}); basicity equivalent 1.01; ^{1}H NMR (DMSO-d_6) δ 6.07 and 5.75 (2 s, 2 H, CH_2=CCH_3), 4.50 (m, 2 H, $COOCH_2$), 3.93 (t, 2 H, CH_2OCO^-), 3.70 (m, 2 H, N^+CH_2), 3.40 (m, 2 H, N^+CH_2), 3.09 (s, 6 H, $N^+(CH_3)_2$), 1.97 (m, 2 H, $N^+CH_2CH_2CH_2$), 1.89 (s, 3 H, CH_2=CCH_3). Anal. Calcd for $C_{15}H_{21}O_4N_3$: C, 58.62; H, 6.89; O, 20.82; N, 13.67. Found: C, 58.68; H, 6.94; O, 20.82; N, 13.66.

3a: yield 75%; mp 129.9 °C; basicity equivalent 1.00; ^{1}H NMR (DMSO-d_6) δ 6.08 and 5.71 (2 s, 2 H, CH_2=CCH_3), 4.32 (m, 2 H, $COOCH_2$), 4.14 (t, 2 H, CH_2OCO^-), 3.58 (m, 2 H, N^+CH_2), 3.41 (m, 2 H, N^+CH_2), 3.08 (s, 6 H, $N^+(CH_3)_2$), 2.07 (m, 2 H, $COOCH_2CH_2CH_2N^+$), 1.89 (s, 3 H, CH_2=CCH_3). Anal. Calcd for $C_{15}H_{21}O_4N_3$: C, 58.62; H, 6.89; O, 20.82; N, 13.67. Found: C, 58.70; H, 6.88; O, 20.79; N, 13.61.

3b: yield 68%; mp 118–119 °C; basicity equivalent 1.01; ^{1}H NMR (DMSO-d_6) δ 6.08 and 5.71 (2 s, 2 H, CH_2=CCH_3), 4.14 (t, 2 H, $COOCH_2$), 3.93 (t, 2 H, CH_2OCO^-), 3.39 (m, 2 H, N^+CH_2), 3.27 (m, 2 H, N^+CH_2), 3.03 (s, 6 H, $N^+(CH_3)_2$), 2.06 (m, 2 H, $COOCH_2CH_2CH_2N^+$), 1.98 (m, 2 H, $COOCH_2CH_2CH_2N^+$), 1.89 (s, 3 H, CH_2=CH_3). Anal. Calcd for $C_{16}H_{23}O_4N_3$: C, 59.86; H, 7.21; O, 19.91; N, 13.07. Found: C, 59.77; H, 7.27; O, 20.13; N, 12.97.

4b: yield 70%; mp 111.4 °C; basicity equivalent 0.98; ^{1}H NMR (DMSO-d_6) δ 6.03 and 5.70 (2 s, 2 H, CH_2=CCH_3), 4.25 (t, 2 H, $COOCH_2$), 3.91 (t, 2 H, CH_2OCO^-), 3.79 and 3.70 (m, 4 H, CH_2OCH_2), 3.46 (m; 2 H, $N^+CH_2CH_2O$), 3.25 (m, 6 H, $N^+(CH_2)_3$), 1.87 (s + m, 5 H, CH_2=CCH_3 + $N^+CH_2CH_2CH_2$), 1.15 (t, 6 H, $N^+(CH_2CH_3)_2$). Anal. Calcd for $C_{17}H_{25}O_5N_3$: C, 60.14; H, 7.70; O, 21.08; N, 11.07. Found: C, 60.14; H, 7.72; O, 21.21; N, 11.07.

5a: yield 87%, mp 94–95 °C; basicity equivalent 1.01; ^{1}H NMR (DMSO-d_6) δ 6.02 (m, 1 H, CH_2=$CHCH_2N^+$), 5.65 and 5.59 (2 d, 2 H, CH_2=CH), 4.34 (m, 2 H, CH_2OCO^-), 3.99 (d, 2 H, =$CHCH_2N^+$), 3.51 (m,, 2 H, $N^+CH_2CH_2COO$), 3.02 (s, 6 H, $N^+(CH_3)_2$. Anal. Calcd for $C_{11}H_{15}O_2N_3$: C, 59.71; H, 6.83; O, 14.46; N, 18.99. Found: C, 59.95; H, 6.89; O, 14.31; N, 19.11.

6a: yield 59%; mp 239–240 °C; basicity equivalent 0.99. Anal. Calcd for $C_{13}H_{11}O_2N_3$: C, 64.72; H, 4.60; O, 13.26; N, 17.42. Found: C, 64.71; H, 4.56; O, 13.34; N, 17.53.

6b: yield 40%; mp > 300 °C; basicity equivalent 0.99; ^{1}H NMR (DMSO-d_6) δ 8.94–7.99 (m, 4 H, C_5H_4N), 7.28 (m, 1 H, CH_2=CH), 6.48–6.13 (m, 2 H, CH_2=CH), 4.67 (t, 2 H, CH_2OCO^-), 3.97 (t, 2 H, N^+CH_2), 2.10 (m, 2 H, $N^+CH_2CH_2$). Anal. Calcd for $C_{14}H_{13}O_2N_3$: C, 65.87; H, 5.13; O, 12.53; N, 16.46. Found: C, 65.11; H, 5.04; O, 12.59; N, 16.40.

7a: yield 79%; mp 242–246 °C; basicity equivalent 0.98; ^{1}H NMR (DMSO-d_6) δ 8.90–8.22 (systems AB, J_{AB} = 7.5 Hz, 4 H, C_5H_4N), 7.00 (m, 1 H, CH_2=CH), 6.62–6.00 (m, 2 H, CH_2=CH), 4.75 (t, 2 H, CH_2OCO^-), 4.35 (t, 2 H, N^+CH_2). Anal. Calcd for $C_{13}H_{11}O_2N_3$: C, 64.72; H, 4.60; O, 13.26; N, 17.42. Found: C, 64.71; H, 4.54; O, 13.50; N, 17.35.

7b: yield 94%; mp 213.7–217.6 °C; basicity equivalent 0.83; ^{1}H NMR (DMSO-d_6) δ 8.95–8.19 (systems AB, J_{AB} = 7.5 Hz, 4 H, C_5H_4N), 6.98 (m, 1 H, CH_2=CH), 6.58–5.96 (m, 2 H, CH_2=CH), 4.55 (t, 2 H, CH_2OCO^-), 3.97 (t, 2 H, N^+CH_2), 2.20 (q, 2 H, $N^+CH_2CH_2$). Anal. Calcd for $C_{14}H_{13}O_2N_3$: C, 65.87; H, 5.13; O, 12.53; N, 16.46. Found: C, 65.64; H, 5.14; O, 13.53; N, 15.88.

8a: yield 96%; mp 183–185 °C; basicity equivalent 1.00; ^{1}H NMR (DMSO-d_6) δ 9.27–8.25 (m, 3 H, C_5H_3N), 7.32–5.88 (m, 3 H, CH_2=CH), 5.05 (t, 2 H, CH_2OCO^-), 4.70 (t, 2 H, N^+CH_2), 3.10 (s, 3 H, $C_5H_3NCH_3$). Anal. Calcd for $C_{14}H_{14}O_2N_3$: C, 65.61; H, 5.51; O, 12.49; N, 16.40. Found: C, 65.69; H, 5.17; O, 12.93; N, 16.54.

8b: yield 75%; basicity equivalent 0.98; ^{1}H NMR (DMSO-d_6) δ 9.26–8.20 (m, 3 H, C_5H_3N), 7.30–5.82 (m, 3 H, CH_2=CH), 4.79 (t, 2 H, CH_2OCO^-), 4.21 (t, 2 H, N^+CH_2), 3.03 (s, 3 H, $C_5H_3NCH_3$), 2.40 (m, 2 H, $N^+CH_2CH_2$). Anal. Calcd for $C_{15}H_{16}O_2N_3$: C, 66.90; H, 5.61; O, 11.88; N, 15.60. Found: C, 66.69; H, 5.63; O, 12.41; N, 15.56.

9a: yield 86%; mp 186–187 °C (ΔH = 186 J·g^{-1}); basicity equivalent 1.01; ^{1}H NMR (DMSO-d_6) δ 9.62–8.04 (m, 3 H, $NC_3H_3N^+$), 7.50 (m, 1 H, CH_2=CH), 6.15–5.69 (m, 2 H, CH_2=CH), 5.60 (m, 4 H, $N^+CH_2CH_2OCO^-$). Anal. Calcd for $C_{11}H_{10}O_2N_4$: C, 57.39; H, 4.37; O, 13.90; N, 24.33. Found: C, 57.68; H, 4.38; O, 13.50; N, 24.82.

9b: yield 97%; mp 113 °C; basicity equivalent 0.99. Anal. Calcd for $C_{12}H_{12}O_2N_4$: C, 59.00; H, 4.95; O, 13.10; N, 22.94. Found: C, 59.28; H, 4.96; O, 13.11; N, 23.38.

(c) Free-Radical Polymerization of the Zwitterionic Monomers. A Pyrex glass ampule containing calculated amounts of monomer, AIBN, DMF, or DMSO as solvent (see Table II) was degassed by three successive freezing–vacuum cycles and finally kept under a slight pressure of argon. It was then immersed in a Lauda thermostat at 60 ± 0.1 °C for a given time (Table I). In most cases, the homogeneous reaction medium was precipitated into a large excess of tetrahydrofurfurylic or furfurylic alcohols for aliphatic and heterocyclic monomers, respectively. The polymer, recovered by filtration, was then thoroughly washed in methanol at ~50 °C under vigorous stirring for 3 h and dried under vacuum at 50 °C. The lack of any residual monomer was checked by thin-layer chromatography (Merck silica gel 60-F-254) by using DMF or TFE as deposition solvents and methanol or TFE as eluant: R_f = 0.34, 0.28, and 0.31 for the monomers **2a**, **8a**, and **9a**, respectively, and R_f = 0 for the corresponding polymer with TFE as eluant, for instance.

In the case of the allylic monomer **5a**, the DMSO solution was concentrated by rotary evaporation and then precipitated into chloroform. The insoluble product was filtered, dried, and redissolved in water; after dialysis for 2 or 3 days using Spectrapor membrane of molecular weight cutoff 1000, the solution was finally freeze-dried; no polymer may be recovered.

(d) Acidic Hydrolysis of Poly(7a). A suspension of 2.4 g of the finely ground polymer in 20 mL of 5 N HCl was heated under reflux between 0.5 and 5 h. After being cooled, the clear homogeneous solution was exhaustively dialyzed against distilled water by using Spectrapor membrane of molecular weight cutoff 1000. When a pH value of ~6 was reached (2–3 days), the polymer was recovered by freeze-drying (yield of ~65%), and further dried under vacuum over P_2O_5 at 50 °C.

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