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Poly(ammonium alkoxydicyanoethenolates) as New Hydrophobic and Highly Dipolar Poly(zwitterions). 2. Mechanistic Aspects of the Polymerization

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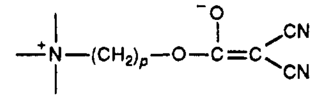
ABSTRACT: Some mechanistic aspects of the polymerization of 2,2-dicyano-1-[2-(2-(methacryloyloxy)ethyl)dimethylammonio)ethoxy]ethenolate were studied to check the possible influence of the highly dipolar lateral zwitterionic group ($\mu \simeq 26$ D) on the polymerization of this methacrylate. Kinetics of the free-radical polymerization in homogeneous dimethylformamide (DMF) solution were analyzed by calorimetry. The molar heat of polymerization, $\Delta H_{p,0} = -58$ kJ·mol^{-1}, is very similar to those generally observed for alkyl methacrylates. The increase of the activation parameters E_a and A derived from the overall rate constant K ($K = A\exp(-E_a/RT) = (k_p^2 f k_d/k_t)^{0.5}$) observed in the presence of preformed poly(zwitterion) in the reaction medium ($E_a = 71 \pm 2$ kJ·mol^{-1}, ln $A = 19.5 \pm 1$ (A in (L·mol^{-1})$^{0.5}$·s^{-1}) with respect to blank experiments ($E_a = 61 \pm 2$ kJ·mol^{-1}, ln $A = 16 \pm 0.5$ (A in (L·mol^{-1})$^{0.5}$·s^{-1}) is not compatible with genuine template effects. Stereoregularity of the radical poly(zwitterions) (^{1}H NMR of the α-CH$_3$ backbone at 400 MHz) is barely sensitive to temperature within the range −20 to +140 °C and to solvent effects (trifluoroethanol, NaSCN (3 M) aqueous solution): the chains are significantly less syndiotactic ($(mm) = 0.09 \pm 0.02$, $(mr) = 0.44 \pm 0.04$, $(rr) = 0.47 \pm 0.05$) than PMMA. Anionic polymerization of the zwitterionic monomer may be initiated by fluorenyllithium in DMF solution at −40 °C: it results in heterotactic polymers ($(mm) = 0.22$, $(mr) = 0.58$, $(rr) = 0.20$), in sharp contrast with methyl methacrylate, probably as a result of strong specific ion–dipole interactions between the zwitterionic groups and the terminal reactive ion pair of the growing chain in the transition state.

Introduction

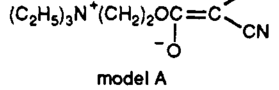
In the first part of these studies we present an overview of the free-radical polymerization of a series of new zwitterionic monomers of the ammonium alkoxydicyanoethenolate type:[1]



$$-\overset{+}{N}-(CH_2)_p-O-\overset{\overset{-}{O}}{\overset{|}{C}}=C(CN)_2 \qquad p = 2, 3$$

Their stable highly dipolar hydrophobic polymers appear quite promising with respect to a variety of both basic and technological purposes, ranging from the analysis of salt effects on the morphological and hydrodynamic behavior of zwitterionic chains in dipolar aprotic solvents[2] to the development of new materials of potential interest in the field of electrets and of host–guest chemistry for polar species (salts, dyes for nonlinear optics), for instance.

As previously shown, the free-radical polymerization of these zwitterionic monomers in homogeneous solution in dimethylformamide (DMF) is straightforward and currently leads to high molecular weights,[1] especially in the methacrylic series. Because of the very high dipole moment of the zwitterionic lateral group ($\mu = 26.0$ D for model compound A as measured in trifluoroethanol solution[3]), strong dipole–dipole interactions between the growing macroradicals and the monomer or the preformed chain for high-conversion experiments may result in association phenomena, quite analogous to the well-known template polymerization.[4,5] Template effects occur essentially in solution whenever the polymeric matrix and the monomer or the growing chain show different and complementary chemical structures allowing the development of strong specific interactions, such as acid–base or hydrogen-bonding interactions in most cases.[4-6] However, they have already been assumed for systems involving polymeric matrix and monomer of identical structure (bulk polymerization of acrylonitrile at low temperature,[7] for instance), and they cannot be ruled out a priori for our zwitterionic system where dipolar interactions are likely of quite unusual strength: a rough oversimplified quadrupole calculation shows that the energy difference between the parallel and antiparallel conformations for a pair of the zwitterionic models separated by 5–6 Å (no steric hindrance for such an approach distance according to Corey–Pauling–Koltun molecular models) in DMF ($\epsilon = 36.7$ at 25 °C) is about $3 \pm 0.5\,kT$ at 60 °C, significantly higher than the thermal Brownian motion. Thus, the main purpose of the present work is the research of possible specific features in the polymerization of these zwitterionic monomers which was studied with respect to two complementary viewpoints:

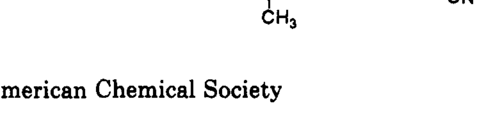


$$(C_2H_5)_3N^+(CH_2)_2O\underset{\underset{O^-}{|}}{C}=C(CN)_2$$

model A

(a) overall kinetics of the radical polymerization, with special emphasis on the determination of activation parameters by dynamic calorimetric measurements and on the potential influence of a zwitterionic matrix; (b) tacticity, with special emphasis on temperature and solvent effects for radical polymerization and on preliminary attempts of anionic polymerization.

For all the studies, the monomer 2,2-dicyano-1-[2-(2-(methacryloyloxy)ethyl)dimethylammonio)ethoxy]ethenolate was chosen as representative of this new class of zwitterions:



$$CH_2=\overset{\overset{CH_3}{|}}{C}-C(=O)O(CH_2)_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}-(CH_2)_2O\overset{\overset{-}{O}}{\overset{|}{C}}=C(CN)_2$$

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The results are critically discussed within the general framework of the much studied polymerization of alkyl methacrylates.

Experimental Section

Solvents, Monomers, and Reagents. Dimethylformamide (DMF) was twice vacuum distilled over CaH_2 and stored under argon over 4-Å molecular sieves in a Schlenk vessel: its water content (Karl Fischer titration) is about 30 ppm. Trifluoroethanol (TFE) was purified according to the literature.[8] Tetrahydrofuran (THF) was twice distilled under argon from its solution of sodium benzophenone dianion directly into a Schlenk vessel. Methyl methacrylate (MMA) was twice vacuum distilled over CaH_2 just before use. 2,2-Dicyano-1-[2-(2-(methacryloyloxy)ethyl)dimethylammonio)ethoxy]ethenolate (I) was prepared as previously described[1] and crystallized from water–methanol (1 vol/1 vol) solution. Azobis(isobutyronitrile) (AIBN) and benzoyl peroxide (Bz_2O_2) were crystallized from methanol and chloroform/methanol, respectively. 4,4′-Azobis(4-cyanovaleric acid) (ACVA) was recrystallized according to a literature procedure.[9] *tert*-Butyl peroxide (TBPO) (Aldrich, 98%), lithium borohydride (Aldrich, 2 M solution in THF), and sodium borohydride (Aldrich, 0.5 M solution in diglyme) were used as received. Solutions of lithium and sodium fluorenyl in THF (0.4–0.6 M) were prepared by metalation of fluorene by lithium and sodium naphthalene[10] and titrated against acetanilide.

Radical Polymerization of the Zwitterionic Monomer I in Homogeneous Solution. Polymerizations in DMF solution at various temperatures were carried out at constant reagent concentrations: $[M] = 0.8\ mol{\cdot}L^{-1}$, $[initiator] = 4 \times 10^{-3}\ mol{\cdot}L^{-1}$. For the higher temperature range (30–130 °C), they were initiated by the thermal decomposition of initiators well adjusted to the isothermal reaction conditions: TBPO/130 °C, Bz_2O_2/90 °C, AIBN/30–60 °C. For the lower temperature range (0 to −20 °C), they were initiated by photolysis of AIBN on a home-built photopolymerization device (Hanovia XBo mercury vapor–xenon lamp) allowing the use of quartz cells thermostated by an external Lauda cryostat, as detailed elsewhere.[11] In all cases, the polymer samples were recovered, purified, and dried as previously described.[1] Yields in the range 10–70% are currently obtained for polymerization times between 2 and 18 h, except for the run performed at 30 °C, where conversion reaches 53% after 6 days of polymerization.

The experimental conditions of radical polymerizations carried out at 60 °C in various solvents are detailed further in the text; see Results and Discussion.

Anionic Polymerization of MMA and Monomer I. All polymerizations were performed under an argon pressure of about 30–40 Torr in an all-Pyrex glass reactor, allowing the use of vacuum and argon sweeping cycles. DMF and the monomer and initiator solutions were introduced under argon from Schlenk vessels or through self-sealing rubber caps by using a syringe technique. After neutralization of the DMF impurities by a few drops of the initiator solution (the orange end point occurs after neutralization of the equivalent of about 30 ppm of H_2O in the medium), the polymerization was carried out by dropwise addition of the precooled monomer (either pure for MMA or a 25% w/v solution in DMF for monomer I) to the solution of the initiator kept under vigorous stirring at the desired temperature; see Results and Discussion for the detailed experimental conditions (monomer and initiator concentrations, temperature, and time). The polymerization was stopped by neutralization of the reaction medium by a few drops of acetic acid, and the polymer was then recovered and purified as usual.[1]

Polymerization Kinetics of Monomer I by Differential Scanning Calorimetry. DMF solutions of the monomer on the one hand and of AIBN + preformed polymer (in the case of template polymerizations) on the other hand were prepared separately at the desired concentrations and then transferred into test tubes fitted with self-sealing rubber caps allowing a thorough degassing by three freeze–thaw cycles combined with vacuum–argon alternation at freezing temperature. The test tubes were then placed into a glovebox under argon, and O-ring stainless steel large-volume pans were filled with a total volume of 50 μL of the initiator and monomer solutions in known ratio (5–10 mg of pure reagents). These pans were sealed in the glovebox just before polymerization. Each pan was checked for tightness by weighing before and after the DSC measurements, which were systematically run at least in duplicate.

Polymerizations were performed using a Perkin-Elmer DSC-4 calorimeter interfaced with a computer data station, after previous calibration for temperature and enthalpy (heating rate of 10 $°C{\cdot}min^{-1}$; indium, $T_m = 156.6\ °C$, $\Delta H_m = 28.51\ J{\cdot}g^{-1}$; gallium, $T_m = 29.8\ °C$, $\Delta H_m = 79.95\ J{\cdot}g^{-1}$). The dynamic experiments were carried out at scan speeds in the range 1–5 $°C{\cdot}min^{-1}$ from 30 up to 140 °C with an empty pan as reference. The isothermal experiments were performed at a preset temperature (55–70 °C) reached from 30 °C at a heating rate of 40 $°C{\cdot}min^{-1}$, using a reference pan filled with 50 μL of an AIBN solution in DMF at the same concentration as that of the measurement pan. When no more polymerization was apparent from the evolved heat record, a heating program up to 140 °C (5 $°C{\cdot}min^{-1}$) was applied to perform quantitative monomer conversion.

Physical Characterization of Polymers. Molecular weights were measured by light scattering in DMF solution as previously described.[1] Molecular weight distributions were estimated by size exclusion chromatography using a GPC apparatus fitted with a set of five columns of polystyrene beads from Polymer Laboratories (PL gel) (one mixed + five 10^5–500 Å), after calibration with standard polystyrenes. The solvents were THF at 25 °C and *N*-methylpyrrolidone/10^{-2} M LiBr at 80 °C for PMMA and the poly(zwitterion), respectively.

For stereoregularity measurements, ^1H NMR spectra were recorded on a Bruker AM-400 (400 MHz) using 1% w/v polymer solutions in DMSO-d_6 at 140 °C. The chemical shifts are referred to DMSO fixed at 2.50 ppm. The α-CH_3 backbone pattern was deconvoluted using the LINESIM program (Bruker), assuming Gaussian shape for the individual resonance peaks and allowing small deviations (≤0.02 ppm) in their characteristic chemical shifts to optimize the fit between the observed and the simulated spectrum.

Results and Discussion

Kinetics of the Free-Radical Polymerization of the Zwitterionic Monomer I. A prerequisite for the study of polymerization kinetics by calorimetry is the knowledge of the molar enthalpy of polymerization $\Delta H_{p,0}$. It was determined by dynamic DSC experiments carried out at various scan speeds β in the range 1–5 $°C{\cdot}min^{-1}$ and for various monomer (0.5–0.75 $mol{\cdot}L^{-1}$) and initiator (0.01–0.02 $mol{\cdot}L^{-1}$) concentrations. The shape of the thermograms recorded between 30 and 140 °C depends upon the solution composition and the scan speed. For a constant scan speed (1 or 2 $°C{\cdot}min^{-1}$) the exothermic peak (both its onset and its maximum) shifts toward lower temperature upon increasing the initiator concentration from 1×10^{-2} to $2 \times 10^{-2}\ mol{\cdot}L^{-1}$ at constant monomer concentration (0.75 $mol{\cdot}L^{-1}$) or upon increasing the monomer concentration from 0.50 to 0.75 $mol{\cdot}L^{-1}$ at a constant initiator concentration ($10^{-2}\ mol{\cdot}L^{-1}$). For a given concentration in reagents, increasing the scan speed results simultaneously in a shift of the exothermic peak toward higher temperature and in a significant decrease of its area, which is a direct measure of the total heat evolved in the system, ΔH_p; see Figure 1 for $[M]_0 = 0.5\ mol{\cdot}L^{-1}$ and $[AIBN]_0 = 10^{-2}\ mol{\cdot}L^{-1}$, for instance. All these characteristic features are quite common in the DSC dynamic studies of radical polymerization.[12]

The determination of a reliable value of the heat of polymerization $\Delta H_{p,0}$ implies extrapolation of the experimental data ΔH_p to zero scan speed for systems containing high enough initiator:[12,13] underestimated ΔH_p values, which correspond to incomplete conversion of the monomer, are generally ascribed to premature exhaustion of the initiator (dead-end polymerization conditions as defined by Tobolsky[14]). This behavior may be clearly seen through the dependence of the experimental ΔH_p values

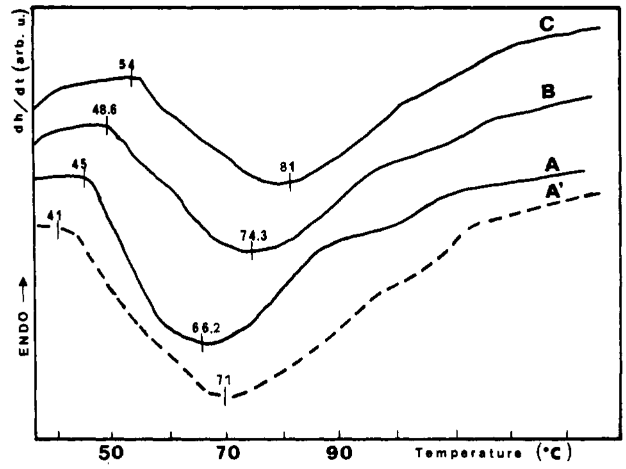


Figure 1. Typical DSC thermograms of the zwitterionic monomer polymerization: $[M]_0 = 0.5$ mol·L^{-1}; $[AIBN]_0 = 0.01$ mol·L^{-1}. Blank experiments: (A) $\beta = 1$ °C·min^{-1}; (B) $\beta = 2$ °C·min^{-1}; (C) $\beta = 3$ °C·min^{-1}. Template experiment: (A') $[P]_0 = 0.2$ mol·L^{-1}, $\beta = 1$ °C·min^{-1}.

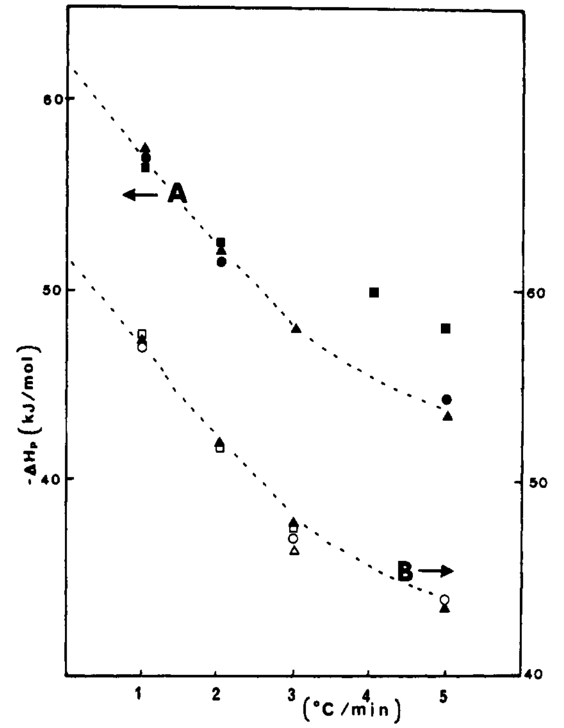


Figure 2. Influence of the scan speed β on the experimental total heat of polymerization ΔH_p. Curve A, blank experiments with $[M]_0 = 0.75$ mol·L^{-1} and $[AIBN]_0 = 0.01$ mol·L^{-1} (●); $[M]_0 = 0.75$ mol·L^{-1} and $[AIBN]_0 = 0.02$ mol·L^{-1} (■); and $[M]_0 = 0.5$ mol·L^{-1} and $[AIBN]_0 = 0.01$ mol·L^{-1} (▲). Curve B, template experiments with $[M]_0 = 0.5$ mol·L^{-1}, $[AIBN]_0 = 0.01$ mol·L^{-1}, and $[P]_0 = 0$ (▲), $[P]_0 = 0.1$ (△), $[P]_0 = 0.2$ (○), and $[P]_0 = 0.3$ mol·L^{-1} (□).

upon the initiator concentration, which is negligible at low scan speeds ($\beta = 1$ or 2 °C·min^{-1}) but quite significant at higher ones ($\beta = 4$ or 5 °C·min); see curve A in Figure 2. Moreover, the experimental data have to be corrected for the heat of decomposition of the initiator ΔH_d ($\Delta H_d = -208.5$ kJ·mol^{-1} for AIBN in DMF[12]), which contributes slightly to the total heat evolved. Finally, three series of scanning experiments lead to a most probable value:

$$\Delta H_{p,0} = (\Delta H_p - \Delta H_d[\mathrm{AIBN}]_0/[\mathrm{M}]_0)_{\beta\to 0} = -58.0 \pm 1\ \mathrm{kJ{\cdot}mol^{-1}}$$

Comparison with literature data for analogous polymerizations in DMF solution[12,13] shows that for a constant monomer concentration of 0.75 mol·L^{-1},[1] the minimum AIBN concentration required to obtain reliable data for the extrapolation procedure depends, as expected, on the monomer structure: it is as high as 0.05 mol·L^{-1} for 2-vinylpyridine,[13] of about 0.01 mol·L^{-1} for *N*-vinylpyrrolidone[12] as for our system.

Table I
Initial Overall Rate Constants *K* of Monomer I Polymerization from Isothermal Thermograms at Various Temperatures[a]

$[M]_0$, mol·L^{-1}	T, °C	10^3K, (mol·L^{-1})$^{-0.5}$·s^{-1}
0.50	55	1.8
	60	2.8
	65	4.0
0.75	60	2.8
	70	5.0
0.50[b]	60	2.0

[a] $[AIBN]_0 = 0.01$ mol·L^{-1}. [b] Isothermal template polymerization with $[P]_0 = 0.2$ mol·L^{-1}.

Isothermal Polymerizations. Isothermal polymerizations were carried out at a constant AIBN concentration of 10^{-2} mol·L^{-1} and for a narrow range of monomer concentrations between 0.3 and 0.75 mol·L^{-1} at 60 °C. The polymerization time was restricted to 1 h, corresponding to a monomer conversion α of about 50%. In most experiments, the total heat evolved calculated from the isotherm and the consecutive scanning experiment (corrected for heating rate effects; see the factor $\Delta H_{p,0}/\Delta H_p$) was systematically lower by about 10% than that expected for quantitative monomer conversion taking into account the $\Delta H_{p,0}$ value previously derived. In such conditions the conversion α was directly measured by the ratio $\Delta h/\Delta H_{p,0}$, where Δh is the heat evolved up to time t calculated from the partial area under the exotherm and normalized to 1 mol. The experimental maximum value of the initial polymerization rates $d\alpha/dt$, which is assumed to be the physically meaningful one, does not correspond to the $(d\alpha/dt)_{t\to 0}$ value at the origin as already observed in similar experiments.[12] The inertia of the microreactor with respect to heat transfer as suggested in the literature[15] or a slow attainment of the steady state may account for an unavoidable time delay which may exceed 1 min. The reaction order in monomer calculated from the variations of the maximum initial polymerization rates with monomer concentration is 0.97, showing thus no significant deviation from the usual first order.

Assuming that the reaction order in initiator I is 0.5 (as generally observed even for template polymerization[5]), the initial monomer consumption may be described according to the classical kinetic equation:[16]

$$\ln \frac{[\mathrm{M}]_0}{[\mathrm{M}]} \equiv \ln\left(\frac{\Delta H_{p,0}}{\Delta H_{p,0} - \Delta h}\right) = K[\mathrm{I}]_0^{0.5}t$$

K is the overall rate constant: $K = (k_p^2 f k_d/k_t)^{0.5}$, where the elementary rate constants k and the initiator efficiency f have their usual meanings.

The K values obtained from polymerizations carried out between 55 and 70 °C are given in Table I.

Activation Parameters of the Polymerization through Scanning Experiments. Scanning experiments provide a straightforward access to the activation parameters of the polymerization by analyzing the thermograms according to the equation[16]

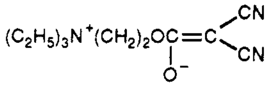
$$K = \frac{dh/dt}{[(\Delta H_{p,0}/\Delta H_p)H - h][\mathrm{I}]^{0.5}} = A \exp\left(-\frac{E_a}{RT}\right)$$

H is the total reaction heat evolved derived from the area

Table II
Activation Parameters for the Blank and Template Polymerization of Monomer I from Scanning Experiments

$[M]_0$, mol·L^{-1}	[AIBN]$_0$, mol·L^{-1}	$[P]_0$, mol·L^{-1}	β, °C·min^{-1}	temp range, °C	conv range, %	ln A, (L·mol^{-1})$^{0.5}$·s^{-1}	E_a, kJ·mol^{-1}
0.75	0.02	0	2	70–92	23–80	16.3	62.4
			4	75–110	15–80	15.9	60.7
	0.01	0	5	76–111	13–90	16.2	61.6
0.5	0.01	0	1	57–86	16–82	15.6	58.9
			2	64–95	16–90	16.4	60.9
			3	67–101	14–88	16.1	60.1
		0.1	3	66–110	11–92	14.2	56.5
		0.2	1	53–85	8–88	18.8	69.0
			3	65–105	9–90	16.3	62.4
			5	66–111	9–88	13.5	54.0
		0.3	1	56–93	10–95	17.8	65.7
			3	67–108	14–92	15.2	59.0
		0.1[a]	1	58–88	12–84	18.3	67.3

[a] Scanning experiment in the presence of the zwitterionic model


$$(C_2H_5)_3N^+(CH_2)_2O\underset{\substack{|\\O^-}}{C}=C(CN)_2$$

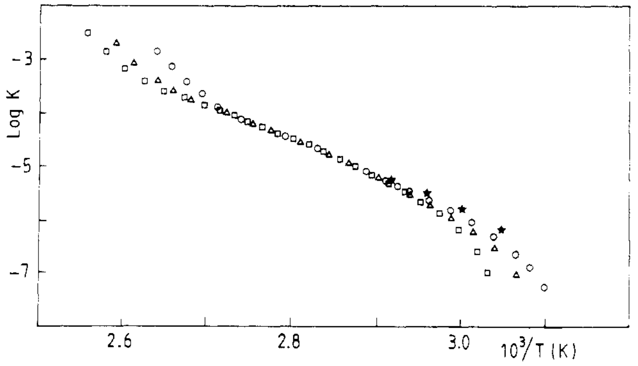


Figure 3. Composite Arrhenius plot of the overall rate constant K for blank polymerizations from scanning and isothermal thermograms. $[M]_0 = 0.5$ mol·L^{-1}; [AIBN]$_0 = 0.01$ mol·L^{-1}. Scanning experiments: β = 1 (○), 2 (△), and 3 (□) °C·min^{-1}. Isothermal experiments: (★) at T = 55, 60, 65, and 70 °C.

Table III
Comparison of Heats of Polymerization $\Delta H_{p,0}$, Activation Parameters E_a and ln A, and Initial Overall Rate Constants K (60 °C) for the Zwitterionic Monomer I and Various Methacrylates ($CH_2{=}C(CH_3)CO_2R$)

R	$-\Delta H_{p,0}$, kJ·mol^{-1}	E_a, kJ·mol^{-1}	ln A, (L·mol^{-1})$^{0.5}$·s^{-1}	10^4K(60 °C/ DMF/ AIBN), (mol·L^{-1})$^{0.5}$·s^{-1}
CH_3[a]	55	76	19.5	3.05
C_2H_5[b]	59			
$(CH_2)_2N$-$(CH_3)_2$[c]		82		
$(CH_2)_2N$[c]	57	98		
C_6H_5[c]	51.5	70	18.3	9.27
$C_6H_4C_6H_5$[d]	72	58	14.4	14.3
zwitterion	58	61	16.0	24.0
+ template	58	71	19.5	21.5

[a] Reference 15. [b] Reference 18. [c] Reference 19. [d] Reference 20.

under the entire DSC curve, h is the reaction heat up to time t or temperature T, and dh/dt is the rate of heat evolution (dt being related to the scan speed $\beta = dT/dt$). E_a is the overall activation energy, A is the preexponential factor, R is the gas constant, and [I] is the instantaneous initiator concentration, which is derived from the relation[16]

$$\ln \frac{[I]_0}{[I]} = \frac{A_d}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E_d}{RT}\right) dT$$

where E_d and A_d are the activation parameters for the monomolecular thermal decomposition of the initiator: $E_d = 142.5$ kJ·mol^{-1} and ln $A_d = 39.5$ (A_d in (L·mol^{-1})$^{0.5}$·s^{-1}) for AIBN in DMF.[12]

From the knowledge of ln A, the overall activation entropy may be calculated according to[17]

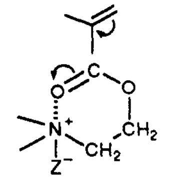
$$\Delta S^{\ddagger} = R\left(\ln A - \ln \frac{k_B T}{\mathbf{h}} - 1\right)$$

where k_B and $\mathbf{h}$ are respectively Boltzmann's and Planck's constants.

The scanning experiments previously used for the determination of $\Delta H_{p,0}$ lead to the Arrhenius plots (ln K versus $1/T$) given in Figure 3. The agreement between the data obtained from experiments run at a constant composition feed and variable scan speeds is excellent, and the plot remains linear over a temperature range of about 30 °C, corresponding to monomer conversion between 10 and 90% (see Table II). Moreover, the K values measured in isothermal conditions between 55 and 70 °C are in good agreement with the corresponding ones derived from the scanning experiments.

The values of ln A and E_a, corrected for the heat of decomposition of AIBN, are given in Table II: they are clearly independent of the experimental conditions (β, $[M]_0$, and [AIBN]$_0$), and their average values are $E_a = 61 \pm 2$ kJ·mol^{-1} and ln $A = 16 \pm 0.5$ (A in (L·mol^{-1})$^{0.5}$·s^{-1}). When compared with some homologous alkyl methacrylates[15,18–20] and especially with its tertiary amino precursor (dimethylamino)ethyl methacrylate (see Table III), the zwitterionic monomer shows a very similar heat of polymerization, but a significantly lower overall activation energy resulting in a higher polymerization rate, much like in the case of biphenyl methacrylate.[20]

The greater reactivity of the zwitterionic species may be tentatively ascribed to an enhanced polarization of its polymerizable double bond as promoted by the cationic site according to the following scheme:



Template Polymerizations. Template polymerizations were performed in the presence of a preformed poly(zwitterion) ($\bar{M}_w = 0.17 \times 10^6$, $[\eta] = 0.156$ dL·g^{-1} in DMF at 60 °C) at constant monomer and initiator concentrations

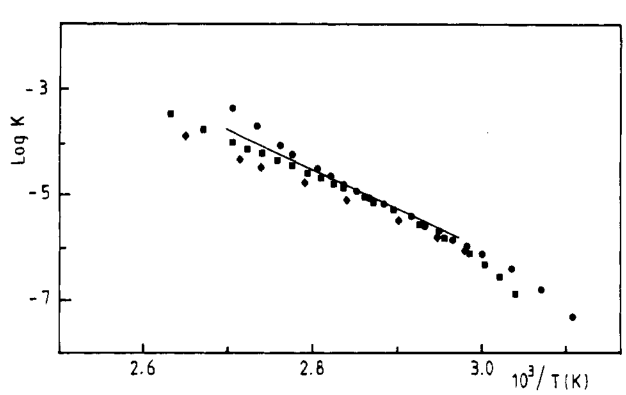


Figure 4. Composite Arrhenius plot of the overall rate constant K for template polymerizations from scanning thermograms. $[\mathrm{M}]_0 = 0.5$ mol·L^{-1}; $[\mathrm{AIBN}]_0 = 0.01$ mol·L^{-1}; $[\mathrm{P}]_0 = 0.2$ mol·L^{-1}; $\beta = 1$ (●), 3 (■), and 5 (◆) °C·min^{-1}.

($[\mathrm{M}]_0 = 0.5$ mol·L^{-1} and $[\mathrm{AIBN}]_0 = 10^{-2}$ mol·L^{-1}) and for various template concentrations in the range 0.1–0.3 mol·L^{-1}, i.e., near or, more likely, over the critical concentration of coil overlap C^* at an average temperature of 60 °C. In such conditions the molecular weight of the matrix chain should have negligible influence on the potential template process.[4,5]

The molar heat of polymerization of the zwitterionic monomer, calculated as previously described through scanning experiments extrapolated to zero scan speed, is not significantly altered by the presence of the matrix polymer, as clearly shown in Figures 1 and 2B. The lack of any template effect however cannot be safely ascertained since the heat of complexing between the growing chain and the template one may be low with respect to the heat of polymerization.[4-6]

The results of isothermal and scanning experiments for template polymerizations are given in Tables I and II, respectively. As shown in Figure 4, the activation parameters E_a and A are a decreasing function of β, in contrast with the previous case of blank experiments. The difference may appear quite puzzling since a matrix polymer is also formed in situ in the blank polymerizations. Such a dependence of the activation parameters with respect to β, noticed, for instance, in the template polymerization of methacrylic acid over poly(2-vinylpyridine) but with a reverse effect[21] (E_a being an increasing function of β), has been ascribed to an increasing lag of the radical concentration with respect to its steady-state value. In our system microphase separation, which occurs in some cases (see further), may result in a higher polymerization rate in the polymer-rich liquid phase and contribute to the observed effects. The E_a and A values extrapolated to zero scan speed may be assumed to be the most reliable. The two series of experiments performed with template concentrations of 0.2 and 0.3 mol·L^{-1} lead to a common value of $E_a = 71 \pm 2$ kJ·mol^{-1} and $\ln A = 19.5 \pm 1$ (A in (L·mol^{-1})$^{0.5}$·s^{-1}).

Comparison with blank experiments (see Table II) points out that the presence of the matrix poly(zwitterion) leads to a weak but physically meaningful increase of both the E_a and A values. Because of opposite contributions of these two activation parameters, the overall rate constants of template polymerization show only slight variations with respect to the blank ones. When the temperature increases from 60 to 90 °C (the range where the experimental data are the most accurate), the characteristic ratio K(template)/K(blank), calculated from the previously extrapolated activation parameters, increases from 0.90 to 1.20 with an isokinetic temperature of about 71 °C.

The influence of the preformed poly(zwitterion) chain on the polymerization of its corresponding monomer may be critically discussed by comparison with the usual template polymerization which arises from strong association of either the monomer or the growing macroradical with the matrix chain through strong specific interactions.[4-6]

Template effects are typical chain effects which appear only over a critical chain length of the matrix polymer (cooperativity effects in the association process[5]): the similar increase of the activation energy obtained with the preformed poly(zwitterion) and with its low molecular weight model compound (triethylammonium ethoxydicyanoethenolate) in similar polymerization conditions (see Table II) is a strong argument for the lack of any genuine template effect in our system.

Template effects generally result in a very strong simultaneous decrease of both the activation energy E_a (of about 25–35 kJ·mol^{-1})[17] and the overall activation entropy ΔS^{*} (of about 90–100 J·mol^{-1}·K^{-1}), except whenever the solvent and the growing chains are in competition for association with the template, which results in a much weaker but still significant decrease of the activation parameters.[17] The reverse effects observed in template polymerization of acrylic and methacrylic acids over poly(oxyethylene) in water solution[22] may be likely considered uncommon. In any case, the simultaneous increase of both E_a (from E_a(blank) $= 61 \pm 2$ kJ·mol^{-1} to E_a(template) $= 71 \pm 2$ kJ·mol^{-1}) and ΔS^{*} calculated at 60 °C (from ΔS^{*}(blank) $= -121 \pm 4$ J·mol^{-1}·K^{-1} to ΔS^{*}(template) $= -92 \pm 8$ J·mol^{-1}·K^{-1}) observed in the zwitterionic system does not appear in favor of usual template effects.

The origin of the observed weak influence of the poly(zwitterion) matrix on the polymerization of its monomer still remains to be defined and could be prospected according to two main lines: (i) modification of the bulk properties of the solvent with respect to viscosity, polarity, and solvation power toward the growing macroradical;[6] (ii) possible microphase separation during the polymerization which may likely induce some kinetic effects: liquid–liquid phase separation was actually observed in specific conditions such as high matrix concentration ($[\mathrm{P}]_0 > 0.2$ mol·L^{-1}) associated with high temperatures ($T > 80$ °C) and high conversions (>70%). This typical behavior is directly related to the phase diagram of the poly(zwitterion) in DMF which shows a characteristic lower critical solution temperature (phase separation occurs on heating up to about 75–80 °C for concentrations between 0.07 and 0.50 mol·L^{-1} for a sample of $\bar{M}_w = 0.22 \times 10^6$), as will be detailed in a further communication.[23]

Finally, it is worth emphasizing that, for an isothermal experiment run at 60 °C ($[\mathrm{M}]_0 = 0.5$ mol·L^{-1}, $[\mathrm{AIBN}]_0 = 10^{-2}$ mol·L^{-1}, $t = 2.5$ h), the presence of the matrix polymer ($[\mathrm{P}]_0 = 0.2$ mol·L^{-1}) does not lead to any significant modification of the molecular weight of the nascent polymer: $\bar{M}_w = 4.5 \times 10^5$ versus 4.6×10^5 for the blank sample. This feature merely means that the poly(zwitterion) chain has a negligible transfer constant toward the corresponding macroradicals.

Tacticity of the Poly(zwitterions) as a Function of Polymerization Conditions. Strong dipolar interactions between the terminal active site of the growing chain and the monomer may induce some preferential conformation in the transition state and thus influence the stereochemistry of the propagation step. Moreover, in the case of anionic polymerization, if possible, specific ion–dipole interactions between the zwitterionic monomer and the terminal ion pair of the growing chain can also play a

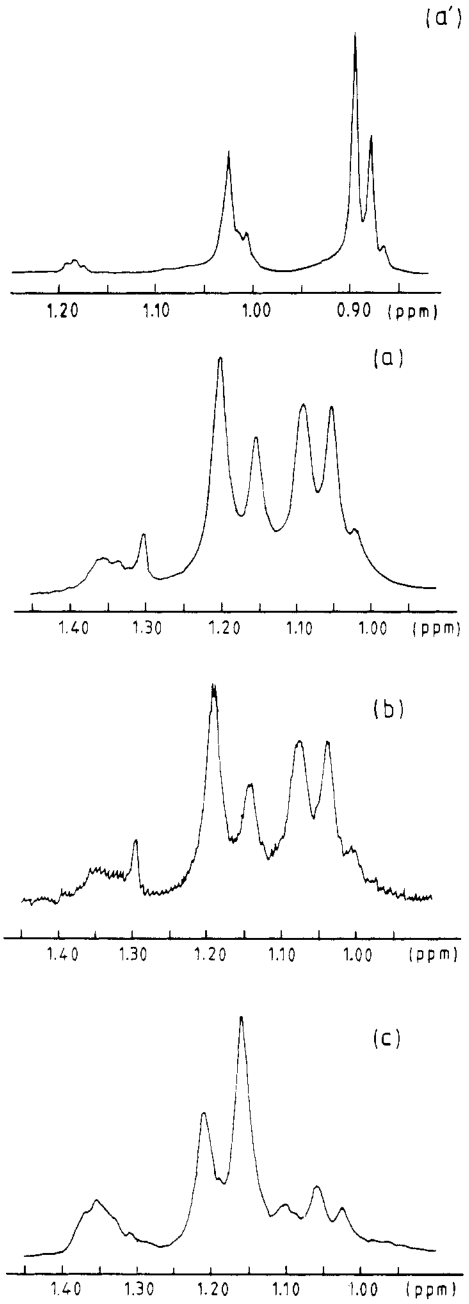


Figure 5. ^{1}H NMR spectra of the α-CH_3 group of PMMA and poly(zwitterions) obtained under various experimental conditions: (a') MMA/AIBN/60 °C/DMF; (a) monomer I/AIBN/60 °C/DMF; (b) monomer I/ACVA/60 °C/TFE; (c) monomer I/fluorenyllithium/−40 °C/DMF.

major role in the stereopropagation. We thus performed an analysis of the tacticity of the poly(zwitterions) obtained either by free-radical polymerization or by anionic polymerization, with special emphasis on temperature and solvent effects for the former process.

Stereoregularity of the Radical Poly(zwitterions). The tacticity of the various poly(zwitterion) samples and of a radical poly(methyl methacrylate) (PMMA, 60 °C, DMF solution) taken as reference was derived from the analysis of the ^{1}H NMR spectra of the backbone α-CH_3 pattern obtained at high field (400 MHz; see Experimental Section); Figure 5 shows some representative spectra. Their clearly apparent resolution in pentads allows us, in principle, to test the two simpler stereopropagation models which assume either the independence (Bernoulli statistics) or the dependence (first-order Markov process) of the probability of forming a meso (m) or a racemic (r) diad on the configuration of the terminal pair of the growing chain.[24,25] The pertinent conditional probabilities in the usual notations are as follows:

$$P(r/m) = 1 - P(m/m) = \frac{(mr)}{2(mm) + (mr)}$$

$$P(m/r) = 1 - P(r/r) = \frac{(mr)}{2(rr) + (mr)}$$

Terminal model:

$$P(r/m) + P(m/r) = 1, \text{ Bernoulli statistics}$$

$$P(m) = 1 - P(r) = (mm) + (mr)/2$$

Penultimate model:

$$P(r/m) + P(m/r) \neq 1, \text{ first-order Markov statistics}$$

The knowledge of the two basic conditional probabilities $P(r/m)$ and $P(m/r)$ derived from the analysis of triad experimental data allows the straightforward calculation of the various pentads according to classical equations.[24,25]

With respect to PMMA, the α-CH_3 pattern of the poly(zwitterion) is shifted toward low field by about 0.16 ppm; because of the lack of well-defined reference isotactic or syndiotactic zwitterionic samples, the most recent pentad assignment for PMMA[26,27] was directly transposed to the poly(zwitterion) of similar backbone. The comparison of the observed and calculated pentads for radical PMMA and a representative poly(zwitterion) obtained under identical conditions is given in Table IV.

In the case of PMMA, the difference between the observed and calculated pentad distributions remain within the experimental error, and, moreover, the deconvolution accuracy is by far too low to allow a reliable choice between the two stereopropagation models leading to quite close distributions. In any case, the PMMA tacticity may be reasonably described in a first approach according to Bernoulli statistics with a characteristic $P(m)$ value of 0.204, in good agreement with the most recent results for radical PMMA obtained at 60 °C in C_6H_6 or toluene:[27] $P(m) = 0.212$. The rather strong deviations from Bernoulli statistics observed more than 15 years ago for identical polymerization conditions[28,29] (DMF, AIBN, 60 °C) may likely arise from uncorrected analysis of poorly resolved spectra (60 MHz).

In the case of the poly(zwitterion) the spectrum resolution is definitely poorer, as clearly shown by a significant broadening of the various peaks and the strong overlapping of the hetero- and syndiotactic triad patterns (see Figure 5): this characteristic feature may likely arise from increased chain rigidity well ascertained by the comparison of the rigidity factors $\sigma = 2.0$ and 3.1 for PMMA and zwitterionic chains, respectively, as derived from dilute-solution studies in DMF.[2] Because of the decreased accuracy on the partial area of the individual peaks (see Figure 6 for a typical deconvolution where the error range is about ±6%) and the lack of sound background for the pentad assignment (see previous assumption), the determination of the poly(zwitterion) tacticities cannot be considered definitive: in most cases, analysis at a triad level would suggest Bernoulli statistics ($P(m/r) + P(r/m) \simeq 1$), and the rather strong deviations observed at the pentad level, even from a first-order Markov process (about 20% for some intense pentads such as ($rrrr$) or ($rrmr$ + $mrmm$) may appear questionable (see Table IV). However,

Table IV
Bernoulli and First-Order Markov Model Fitting for the Radical PMMA and Poly(zwitterion) Obtained at 60 °C in DMF Solution

n-ad	peak	δ, ppm	obsd	Bernoullian trial	first-order Markov
		(A) Radical PMMA			
				$P(m) = 0.204$	$P(m/r) = 0.814$
triad					$P(r/m) = 0.208$
(*mm*)			0.038	0.041	
(*mr*)			0.332	0.325	
(*rr*)			0.630	0.634	
pentad					
(*mmmm*)				0.002	0.001
(*rmmr*)	1+2+3	1.18	0.037	0.026	0.023
(*mmmr*)				0.013	0.011
(*rmrr*)	4			0.206	0.214
(*mmrm*)		1.03	0.254	0.014	0.013
(*rmrm*)	5			0.053	0.056
(*mmrr*)		1.01	0.078	0.053	0.050
(*rrrr*)	6	0.90	0.426	0.402	0.395
(*mrrr*)	7	0.88	0.181	0.206	0.208
(*mrrm*)	8	0.87	0.024	0.026	0.027
		(B) Poly(zwitterion)			
				$P(m) = 0.315$	$P(m/r) = 0.649$
					$P(r/m) = 0.303$
triad					
(*mm*)			0.110	0.099	
(*mr*)			0.414	0.431	
(*rr*)			0.476	0.469	
pentad					
(*mmmm*)				0.010	0.014
(*rmmr*)	1+2+3	1.32	0.138	0.046	0.041
(*mmmr*)				0.043	0.051
(*rmrr*)				0.202	0.187
(*mmrm*)	4	1.19	0.259	0.043	0.044
(*rmrm*)	5			0.093	0.081
(*mmrr*)		1.14	0.155	0.093	0.101
(*rrrr*)	6	1.08	0.265	0.220	0.220
(*mrrr*)	7	1.04	0.126	0.202	0.201
(*mrrm*)	8	1.01	0.057	0.046	0.044

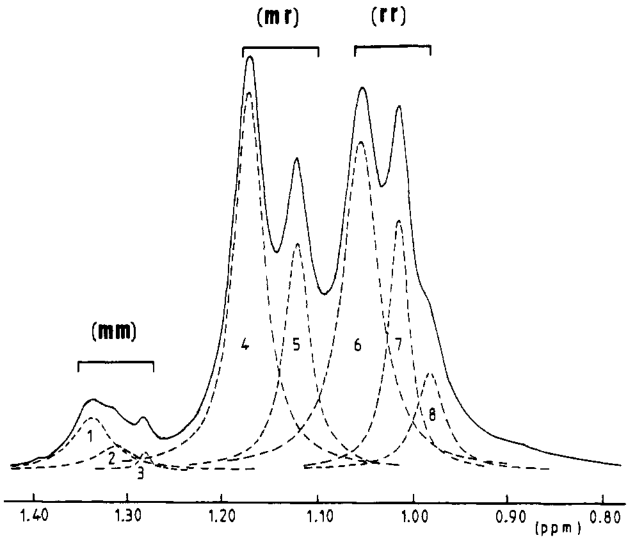


Figure 6. Deconvolution of the ^{1}H NMR spectrum of the α-CH_3 pattern for a typical radical poly(zwitterion) (AIBN/90 °C/DMF).

some general semiquantitative trends may be derived from triad analysis and from the "apparent" $P(m)$ values.

(i) For a polymerization temperature of 60 °C, the poly(zwitterion) appears definitely less syndiotactic (number-average sequence length of syndiotactic blocks $n_r = 3.3$) than PMMA ($n_r = 4.8$) and the amino precursor ($n_r = 4.4$): this may merely arise from the greater steric hindrance of the lateral group, which favors isotactic propagation in the alkyl methacrylate series.[27,30]

Table V
Tacticities of Various PMMA and Poly(zwitterions) Obtained by (A) Radical Polymerization in DMF Solution at Various Temperatures, (B) Radical Polymerization at 60 °C in Various Solvents, and (C) Anionic Polymerization in DMF Solution at Various Temperatures

	(*mm*)	(*mr*)	(*rr*)	$P(m/r)$	$P(r/m)$
	(A) Radical Polymerization/DMF Solution				
130 °C	0.11	0.48_5	0.40_5	0.692	0.374
90 °C	0.07_5	0.43_5	0.49	0.746	0.306
60 °C[a]	0.04	0.33	0.63	0.814	0.208
60 °C	0.11	0.41	0.48	0.651	0.299
30 °C	0.06	0.43	0.51	0.770	0.297
2 °C	0.10_5	0.46_5	0.43	0.691	0.351
−20 °C	0.11	0.44	0.45	0.672	0.325
	(B) Radical Polymerization/60 °C				
TFE	0.14	0.40	0.46	0.582	0.302
H_2O/NaSCN (3 M)	0.17_5	0.39	0.43_5	0.532	0.312
	(C) Anionic Polymerization/DMF Solution				
−40 °C[b]	0.02_5	0.25	0.72_5	0.833	0.147
−40 °C	0.21_5	0.58	0.20_5	0.579	0.587
−40 °C[c]	0.20_5	0.59_5	0.20	0.593	0.601
−10 °C	0.15_5	0.58_5	0.26	0.657	0.529

[a] Data for radical PMMA. [b] Data for anionic PMMA. [c] With fluorenylsodium as initiator.

(ii) Temperature effects between −20 and +140 °C in DMF solution cannot be rationalized since the "apparent" $P(m)$ variations appear randomly scattered; see Table V. We have no satisfactory explanation for this puzzling behavior. However, these effects remain rather small ($(mm) = 0.09 \pm 0.02$, $(mr) = 0.44 \pm 0.04$, and $(rr) = 0.47 \pm 0.05$), in contrast with those observed for PMMA, where syndiotacticity is a decreasing function of temperature whatever the solvent is[28,31] ($P(m)$ increases from 0.18 at −20 °C up to 0.33 at +150 °C in bulk polymerization, for instance[31]).

(iii) The study of solvent effects at a constant temperature of 60 °C shows that, with respect to DMF, stereopropagation in trifluoroethanol and even more in a 3 M NaSCN aqueous solution is characterized by a stronger deviation with respect to the terminal model ($P(r/m) + P(m/r) < 1$) and a simultaneous weak but significant increase of the isotactic triads; see Table V. This feature, in contrast with the quasi-insensitivity of PMMA tacticity with respect to solvent nature,[28,31] may be tentatively correlated with polarity factors and possible variations of the solvation of the active site–monomer complex in the transition state. With respect to the zwitterionic moiety, dipolar interactions in DMF solution turn to strong hydrogen bonding at the anionic site in TFE solution and, finally, to strong specific ion–dipole interactions in aqueous salt solutions.[2,23] Moreover, different radical–solvent or radical–ion interactions cannot be ruled out a priori.[6] On the other hand, the variations of the yields and of the molecular weights of the recovered polymers obtained under otherwise similar reaction conditions suggest potential solvent effects on the polymerization kinetics; see Table VI. Aqueous salt solution allows very fast polymerization and leads to the highest molecular weight, corresponding more likely to a significant increase of the kinetic chain length in this very polar medium rather than to minimum effects of transfer to solvent.

Anionic Polymerization of the Zwitterionic Monomer I. The zwitterionic methacrylate shows solubility properties restricted to highly dipolar aprotic solvents[1] (excluding THF or glymes, for instance) and potential sensitivity toward deprotonation of its quaternary ammonium structure by strong bases (Hoffmann degradation[33]). Its anionic polymerization thus appears rather

Table VI
Solvent Effects on the Radical Polymerization of Monomer I[a]

solvent	initiator[b]	yield, %	$10^{-6}\bar{M}_w$
DMF	AIBN	68	0.40
TFE	ACVA	21	0.39
NaSCN (3 M)/H_2O	ACVA	87	2.35

[a] $[M]_0 = 0.3$ mol·L^{-1}, $[\text{initiator}]_0 = 4 \times 10^{-3}$ mol·L^{-1}, time = 2 h, $T = 60$ °C. [b] $k_d(60\ °C) = 6.34 \times 10^{-6}$ and 8.84×10^{-6} s^{-1} for AIBN[12] and ACVA,[32] respectively.

Table VII
Anionic Polymerization of MMA and of the Zwitterionic Monomer I in DMF Solution Initiated by Fluorenyllithium

monomer	[M], mol·L^{-1}	10^2[I], mol·L^{-1}	T, °C	time, h	yield, %	$10^{-4}\bar{M}_w$
MMA	1.00	1.00	−40	1.75	88	2.98[c]
I	0.35	0.83[a]	−40	1.0	41	1.28
I	0.46	0.92	−40	2.0	30	1.92[d]
I	0.46	1.80[b]	−10	5.0	12	1.19

[a] With fluorenylsodium as initiator. [b] Half of the total initiator solution was added in the medium after a preliminary step of 1 h, where conversion was negligible. [c] With $M_w/M_n = 1.6$ from GPC measurements. [d] With $M_w/M_n = 1.2$ from GPC measurements.

Table VIII
Bernoulli and First-Order Markov Model Fitting for the Anionic PMMA and Poly(zwitterion) Obtained at −40 °C in DMF Solution with Fluorenyllithium

n-ad	peak	obsd	Bernoullian trial	first-order Markov
(A) Anionic PMMA				
			$P(m) = 0.150$	$P(m/r) = 0.833$ $P(r/m) = 0.147$
triad				
(mm)		0.025	0.023	
(mr)		0.250	0.255	
(rr)		0.724	0.723	
pentad				
$(mmmm)$			0.000_5	0.000_7
$(rmmr)$	1+2+3	0.026	0.016	0.017
$(mmmr)$			0.006	0.006
$(rmrr)$	4		0.184	0.178
$(mmrm)$		0.216	0.006	0.006
$(rmrm)$	5		0.033	0.031
$(mrrm)$		0.034	0.033	0.036
$(rrrr)$	6	0.525	0.522	0.527
$(mrrr)$	7	0.179	0.184	0.179
$(mrrm)$	8	0.020	0.016	0.016
(B) Poly(zwitterion)				
				$P(m/r) = 0.579$ $P(r/m) = 0.587$
triad				
(mm)		0.212		
(mr)		0.583		
(rr)		0.205		
pentad				
$(mmmm)$	1	0.046		0.038
$(rmmr)$	2	0.113		0.083
$(mmmr)$	3	0.053		0.103
$(rmrr)$	4			0.139
$(mrmm)$		0.215		0.144
$(rmrm)$	5			0.198
$(mmrr)$		0.368		0.101
$(rrrr)$	6	0.047		0.035
$(mrrr)$	7	0.118		0.099
$(mrrm)$	8	0.085		0.071

problematic, but it was however tested by some preliminary experiments with, as a major goal, the comparison of the tacticities of the radical and anionic samples. Lithium borohydride or sodium borohydride and the corresponding fluorenyl carbanions were selected as initiators in DMF solution for the following reasons:

(i) DMF appears stable toward all these organometallic reagents (no reduction with the weakly reducing borohydride reagents, for instance[33]) and toward the terminal alkali-metal enolate of the growing PMMA chain,[34] at least at low temperature.

(ii) Fluorenyl carbanions are nucleophilic enough to initiate the anionic polymerization of MMA[35] and not basic enough ($pK_{a,\text{fluorene}} = 23$[33]) to promote the Hoffmann degradation of quaternary ammonium structures;[36] the borohydrides are well-known to yield essentially atactic PMMA[37] ($(mm) = 0.22$, $(mr) = 0.53$, and $(rr) = 0.25$ in bulk).

The experimental results of the most representative experiments are given in Table V.

(a) Lithium borohydride and sodium borohydride are quite inefficient initiators of the zwitterionic monomer in DMF solution between −40 and +20 °C.

(b) Fluorenyllithium or -sodium promotes the polymerization, but probably with strong initiator consumption by secondary reactions at temperatures higher than −10 °C (no polymerization at +20 °C). In all cases, including that of MMA (see Table VII), the molecular weights of the polymers are by far higher (more than a factor 2) than the calculated ones ($\overline{DP}_n = [M]/[I] \times \tau$, where τ is the monomer conversion), and the molecular weight distributions are relatively broad ($\bar{M}_w/\bar{M}_n = 1.2$–$1.6$). These characteristic features may be ascribed to slow initiation with respect to fast propagation, as already noticed for MMA in THF solution.[35,38]

The sharp tacticity contrast between PMMA and the poly(zwitterion) obtained under similar conditions (DMF, Li^+, −40 °C) is especially striking and requires further discussion (see Table VIII). PMMA is predominantly syndiotactic and shows here again only weak deviations from the two stereopropagation mechanisms ($P(m/r) = 0.833$ and $P(r/m) = 0.147$). This is in good agreement with most literature data related to anionic PMMA obtained with lithium counterion at low temperatures in weakly dissociating but strongly coordinating solvents like THF or glymes[27] ($(mm) = 0.04$, $(mr) = 0.26$, and $(rr) = 0.70$ in THF at −40 °C with fluorenyllithium, for instance[35]). It is worth emphasizing that in our experimental conditions (high initiator concentration of 1×10^{-2} mol·L^{-1}), the shift from THF ($\epsilon = 9.9$[39] at −40 °C, donicity[40] DN = 83.7 kJ·mol^{-1}) to DMF ($\epsilon = 52.1$ at −40 °C, DN = 111.3 kJ·mol^{-1}), a much more strongly dissociating and better donor solvent, has practically no influence on the chain tacticity, suggesting similar transition states in the propagation step in both solvents. With both Li^+ and Na^+ as counterions, the zwitterionic monomer leads to a predominantly heterotactic chain, which shows significant deviations from a first-order Markov process and looks like PMMA or poly[(dimethylamino)ethyl methacrylate] obtained with bulky counterions and, more especially, K^+ in THF at −78 °C:[27,30,41] $(mm) = 0.11$, $(mr) = 0.53$, and $(rr) = 0.36$ for PMMA and $(mm) = 0.15$, $(mr) = 0.59$, and $(rr) = 0.26$ for poly[(dimethylamino)ethyl methacrylate] polymerized in the presence of octylpotassium,[41] for instance. The formation of heterotactic polymer is of special interest since it implies a higher order of stereoregulation than for isotactic or syndiotactic propagation. The observed difference between PMMA and the poly(zwitterion) clearly shows that strong specific ion–dipole interactions with the terminal ion pair of the growing chain must play a major role in the transition state.

Conclusion

The previous mechanistic studies may suggest some guidelines for future more detailed studies.

Radical polymerization of the zwitterionic monomer I in homogeneous solution does not show any spectacular deviation from the classical behavior of typical alkyl methacrylates, in spite of the unusually high dipole moment of its lateral group. However, template polymerization may be reasonably anticipated, and more systematic studies in two cases would be worthwhile: (i) polymerization over stereoregular isotactic or syndiotactic zwitterionic matrices, the driving force for chain association being the complementarity of the opposite tacticities of the matrix and of the nascent polymer to yield the stereocomplex, as in the well-known case of PMMA[4-6] (this implies the preliminary synthesis of the stereoregular poly(zwitterions) which could be achieved by selective and quantitative quaternization of the stereoregular poly[(dimethylamino)ethyl methacrylates]; (ii) polymerization over anionic or cationic polyelectrolyte matrices, the driving force for chain association being ion–dipole interactions and, here, quite specific to the zwitterionic structure of the monomer I.

Anionic polymerization in homogeneous solution in highly dipolar solvents such as DMF appears feasible and of definite interest with respect to the influence of zwitterion–active site interactions on the stereopropagation process, but optimization of the solvent–initiator systems for the preparation of high molecular weight monodisperse chains may appear a difficult task. On the other hand, the more recently introduced group transfer polymerization method[42] would perhaps prove to be more adjusted to these rather exotic zwitterionic methacrylates or acrylates.

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Registry No. TFE, 75-89-8; AIBN, 78-67-1; DMF, 68-12-2; ACVA, 2638-94-0; NaSCN, 540-72-7; $H_2C{=}C(CH_3)CO_2(CH_2)_2N^+(Me)_2(CH_2)_2OCOC^-(CN)_2$, 109509-78-6; $H_2C{=}C(CH_3)CO_2(CH_2)_2N^+(Me)_2(CH_2)_2OCOC^-(CN)_2$ (homopolymer), 134287-44-8; fluorenylsodium, 3531-83-7.