Articles

Synthesis, Characterization, and Thermal Properties of Poly(trimethylene-1,1-dicarboxylate) Polyelectrolytes

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ABSTRACT: The potassium salt of poly(trimethylene-1,1-dicarboxylic acid), the first member of a new polyelectrolyte family where the carbon backbone is substituted on every third carbon by two carboxylate anions, was obtained by hydrolysis of a monodisperse di-*n*-propyl ester polymer $(CH_2CH_2C(COOnPr)_2)_n$. This precursor can be synthesized by anionic ring-opening polymerization of di-*n*-propylcyclopropane-1,1-dicarboxylate using a polymerization procedure already proved to be living for a similar cyclopropyl monomer. The polyelectrolyte potassium salt was fully characterized by solid-state ^{13}C NMR, FT-IR, elemental analysis, and thermogravimetry (TGA), providing clear evidence for a very selective and clean hydrolysis. The malonate ion substructure on the polymer is very stable and does not decompose below 350 °C. No procedure could be identified to cleanly decarboxylate the polymer to the monosubstituted system. The polymer is very insoluble in water unless high concentrations of potassium hydroxide are used (>1 mol L^{-1}), a behavior consistent with the very high symmetry of the polymer and its high tendency to crystallize.

Introduction

Charged macromolecules (i.e., polyelectrolytes) are particularly important building blocks for the fabrication of supramolecular superstructures. Self-assembly relies essentially on noncovalent forces, and strong electrostatic and hydrophobic/hydrophilic interactions present in polyelectrolytes are particularly efficient at driving and controlling self-assembly processes.[1,2] Metal-ion-directed self-assembly and layer-by-layer deposition of polyelectrolytes are good examples of what can be achieved with relatively simple systems.[3−10] Structured polyelectrolytes like DNA can also be used as platforms for the preparation of nanometer-scale electronic components such as nanowires.[11,12]

Although mostly any polyelectrolyte with the right charge density will work in some applications, control over the dimensions and morphology of the targeted supramolecular structures requires access to more sophisticated macromolecular building blocks of controlled size, functionality, structure, and architecture. Methodologies to obtain such ionic building blocks with perfect control over the location of functional groups on the backbone are particularly critical when a specific correlation of positions for the side substituents is needed or when symmetrical structures have to be obtained. In these cases, existing synthetic and natural polyelectrolytes will often fail, and synthetic polyelectrolytes with very regular structures and/or the ability to selectively complex specific counterions have the potential to considerably expand the range of applications currently available.

In this paper, we want to describe the preparation and characterization of an entirely novel and very symmetrical polyelectrolyte that meets the structural requirements described in the above paragraph. The structure is based on an all-carbon backbone substituted by two carboxylate anions on every third atom alongside the carbon chain. This polymer has a very high symmetry and also the right structure needed to complex metal ions via the bidentate ligand provided by the malonate ion substructure in the repeating unit.

Experimental Part

Materials. Malonic acid (99%, Aldrich), *n*-propanol (99%, Acros), benzene (99%, EM), *p*-toluenesulfonic acid monohydrate (*p*-TsOH (certified, Fisher)), the dimethyl sulfoxide (DMSO) used in the synthesis of **1** (99%, Acros), potassium carbonate (anhydrous, p.a., Acros), 1,4-dioxane (99.9%, Fisher), and potassium hydroxide (certified, 86.6%, Fisher) were commercially available and used without further purification. The synthesis of the sodium thiophenolate initiator and purification of the DMSO solvent used in the polymerization have been described previously.[13−15]

Di-*n*-propyl Malonate Synthesis. A mixture of malonic acid (62.40 g, 0.6 mol), *n*-propanol (72.00 g, 1.2 mol), *p*-toluenesulfonic monohydrate (5.70 g), and benzene (300 mL) in a 1 L flask was heated at reflux for 5 h until the azeotropic mixture had entirely distilled in a Dean−Stark condenser. The resulting solution was cooled to room temperature and washed twice with 40 mL of a saturated potassium carbonate aqueous solution. The organic extracts were evaporated under vacuum, and the residue was distilled (72 °C/1.0 mmHg) to provide a colorless liquid with a yield of 79%. ^1H NMR ($CDCl_3$, 300

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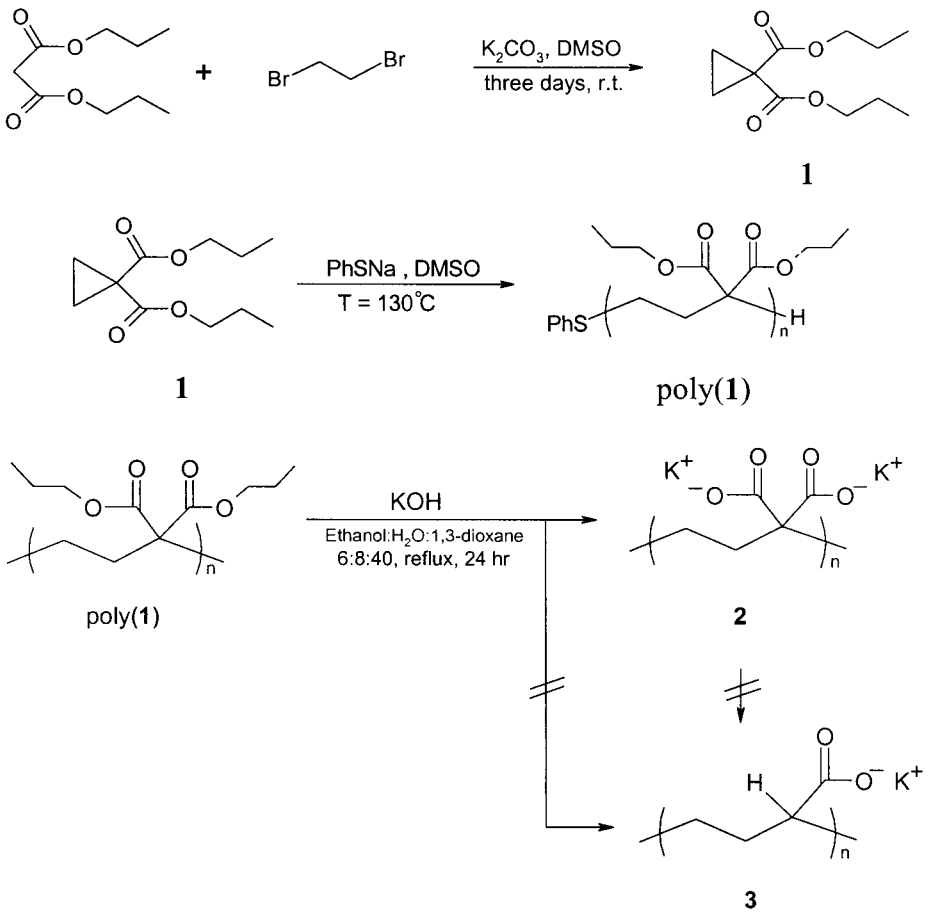
Scheme 1



MHz): δ (ppm) 0.97 (t, 6H, CH_3CH$_2$CH$_2$), 1.68 (m, 4H, CH$_2$CH_2-CH$_3$), 3.39 (s, 2H, CH_2(CO$_2$R)$_2$), 4.12 (t, 4H, COO−CH_2).

Synthesis of Di-*n*-propylcyclopropane-1,1-dicarboxylate (1). A mixture of di-*n*-propyl malonate (94 g, 0.50 mol), 1,2-dibromoethane (197.4 g, 1.05 mol), anhydrous potassium carbonate (410 g, 3.0 mol), and DMSO (560 mL) was stirred vigorously for 3 days at room temperature. 1.0 L of water was added to the resulting mixture, and the obtained solution was extracted with three 400 mL ether fractions. The combined ether extracts were dried over sodium sulfate. The ether was evaporated and the residue distilled under vacuum (74 °C/1.0 mmHg) to yield **1** (87.2 g, yield: 82%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ (ppm) 0.70 (t, 6H, CH_3CH$_2$), 1.19 (s, 4H, cyclopropyl CH_2), 1.43 (m, 4H, CH$_2$CH_2CH$_3$), 3.86 (t, 4H, COO−CH_2). ^{13}C NMR (CDCl$_3$, 300 MHz): δ (ppm) 10.6 (*C*H$_3$), 16.3 (cyclopropyl *C*H$_2$), 22.3 (*C*H$_2$CH$_3$), 28.6 (cyclopropyl *C*), 67.2 (COO−*C*H$_2$), 170.2 (*C*(=O)−O). IR (liquid film): 2970, 2941, 2882, 1734, 1323, 1058, 922, 735 cm^{-1}. Elemental Analysis: $C_{11}H_{18}O_4$ (214.3). Calcd: C, 61.66; H, 8.47. Found: C, 61.75; H, 8.31.

Synthesis of Poly(Di-*n*-propyltrimethylene-1,1-dicarboxylate) (Poly(1)). Sodium thiophenolate (0.68 mg, 0.00052 mol) dissolved in 1.6 mL of DMSO was added into a polymerization tube, and monomer **1** (4.75 g, 0.0222 mol) was introduced thereafter. The mixture in the polymerization tube was purged with nitrogen for 10 min. The polymerization tube was closed and maintained in an oil bath at 130 °C for 24 h. A small drop was taken out of the polymerization mixture in order to evaluate the actual conversion of the monomer by ^{1}H NMR. The polymerization was quenched by adding 1 mL of concentrated hydrochloric acid. 2 mL of chloroform was added to dissolve the precipitated polymer, which was further purified by precipitation into methanol. The obtained white powder was dried in a vacuum oven (yield = 52%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ (ppm) 0.89 (t, 6H, CH_3), 1.63 (m, 4H, COOCH$_2$CH_2-CH$_3$), 1.71 (s, 4H, backbone CH_2), 4.05 (t, 4H, COOCH_2). ^{13}C NMR (CDCl$_3$, 300 MHz): δ (ppm) 10.3 (*C*H$_3$CH$_2$CH$_2$O), 21.8 (CH$_3$*C*H$_2$CH$_2$O), 26.5 (backbone *C*H$_2$), 56.9 (backbone *C*), 66.8 (COO−*C*H$_2$), 170.8 (*C*(=O)−O). IR (KBr): 2973, 1734, 1278, 1199, 1180, 1058, 936 cm^{-1}. Elemental Analysis: $(C_{11}H_{18}O_4)_n$ $(214.3)_n$. Calcd: C, 61.66; H, 8.47. Found: C, 61.96; H, 8.19.

Synthesis of the Dipotasium Salt of Poly(trimethylene-1,1-dicarboxylic acid) (2). A potassium hydroxide aqueous solution (1.2 g KOH in 8 mL solution) was added to a solution of poly(**1**) (1.02 g) in 40 mL of 1,4-dioxane. The mixture was heated at reflux, and ethanol was added dropwise until the solution became homogeneous (about 6 mL). The reflux was then maintained for an additional 24 h. The solvents were evaporated, and the residual solid was dissolved in 10 mL of water. The hydrolyzed polymer **2** was recovered by precipitation into 250 mL of methanol and further dried under vacuum (80 °C for 16 h), yielding 1.07 g of a slightly yellow powder.

Measurements. Solid-state and solution ^{13}C NMR experiments were conducted on 300 MHz Bruker DSX and DPX spectrometers, respectively. CDCl$_3$ was used as the solvent. IR spectra were recorded on either a Nicolet FT-IR 205 or a Perkin-Elmer 2000 FT-IR spectrometer. The gel permeation chromatography (GPC) experiment was performed in THF at room temperature using a PL LC 1120 pump, a Waters R403 differential refractometer detector, and three PLgel columns (10^5, 10^4, and 10^3 Å). The system was calibrated with poly(methyl methacrylate) standards. The vapor pressure osmometry (VPO) experiment was performed in toluene at 51 °C using a Jupiter VPO 833 osmometer. Thermal decompositions were evaluated by thermogravimetric analysis (TGA) using a SETARAM TGC 85 apparatus (heating rate: 10 K min^{-1}, nitrogen). Elemental analyses were carried out in the Microanalysis Laboratory of the University of Massachusetts—Amherst.

Results and Discussion

Polymer Synthesis. The synthetic procedure used to obtain polyelectrolyte **2** involves three steps (mono-

mer synthesis, polymerization of the monomer, and hydrolysis of the obtained polymer) which are summarized in Scheme 1. The monomer, di-*n*-propyl cyclopropane-1,1-dicarboxylate (**1**), was obtained in high yield (two steps, global yield: 65%) from readily available commercial reagents according to a procedure that had been known for more than a century and recently modified in our group in order to reach the analytical purity requested by anionic polymerization.[13,14] The expected structure and purity were confirmed by ^{1}H NMR, ^{13}C NMR, FT-IR, and elemental analysis. The polymerization itself is based on previous results reported by us on the ring-opening polymerization of cyclopropane-1,1-dicarboxylates.[14,15] The di-*n*-propyl ester was chosen rather than previously described diethyl and diisopropyl esters because of the higher solubility of the polymer in solvents suitable for postpolymerization reactions such as the hydrolysis reported here. Monomer **1** was polymerized using sodium thiophenolate as an initiator (2.36 mol %) and a small amount of DMSO to dissolve the initiator. The polymerization was carried out at 130 °C for 24 h, conditions that have been identified previously as suitable for comparable monomers.[15] An actual monomer conversion of 90% was determined by comparing the intensities of the peaks corresponding to the polymer backbone CH_2 (1.7 ppm) and monomer cyclopropyl CH_2 (1.4 ppm), respectively, on the ^{1}H NMR spectrum of the raw polymerization mixture. After a purification step based on a dissolution−precipitation process (solvent = chloroform, nonsolvent = methanol), a global yield of 52% was obtained. Several alternative experimental conditions for the precipitation process were investigated, without any major improvement in the recovery of the final polymer. Poly(**1**) was obtained as a slightly yellow powder, soluble in most traditional organic solvents such as toluene, benzene, chlorobenzene, THF, acetone, chloroform, dichloromethane, and carbon tetrachloride but insoluble in saturated hydrocarbon solvents such as pentane and cyclohexane. Structural data obtained by ^{1}H NMR, ^{13}C NMR, and IR are in perfect agreement with the expected structure. The number-average molecular weight $\bar{M}_n$ was determined for the precipitated polymer by GPC, VPO, and end group analysis using quantitative ^{1}H NMR (ratio of aromatic protons on the phenylthio end group (7.1−7.4 ppm) and OCH_2− protons on the propyl ester groups of the repeating units (4.1 ppm)). All three techniques agree very well: 8970 (VPO), 9000 (GPC, calibrated with PMMA standards), and 8330 (NMR). These numbers are consistent with a theoretical $\bar{M}_n$ of 8090 calculated on the assumptions of a living polymerization and a conversion of 90%. A low polydispersity index ($\bar{M}_w/\bar{M}_n$) of 1.10 was measured by GPC. The low recovery obtained during the workup (58%) makes it difficult to reach a completely unambiguous explanation for these results: the monodispersity and molecular weight can either be rationalized on the basis of a living polymerization or result from some fractionation taking place during the precipitation step.

In a last step, poly(**1**) was hydrolyzed in 1,4-dioxane in the presence of excess potassium hydroxide. Polyelectrolyte **2** was obtained as a slightly yellow powder insoluble in all tested organic solvents, including chloroform, dichloromethane, acetone, DMSO, benzene, THF, cyclohexane, and *n*-hexane. More surprisingly, **2** also does not dissolve in water at neutral pH. To check whether the insolubility arises from possible transfer of protons to the polymer at neutral pH, sodium hydroxide or potassium hydroxide was progressively added to H_2O/polymer **2** suspensions up to a pH of 14 at room temperature and 80 °C. When sodium hydroxide was used, the mixture remained as a suspension in the entire pH range from 7 to 14, even at high temperature. When potassium hydroxide was used instead, a clear solution could be obtained when the pH and temperature were above 13 and 80 °C, respectively. Otherwise, the polymer remained insoluble.

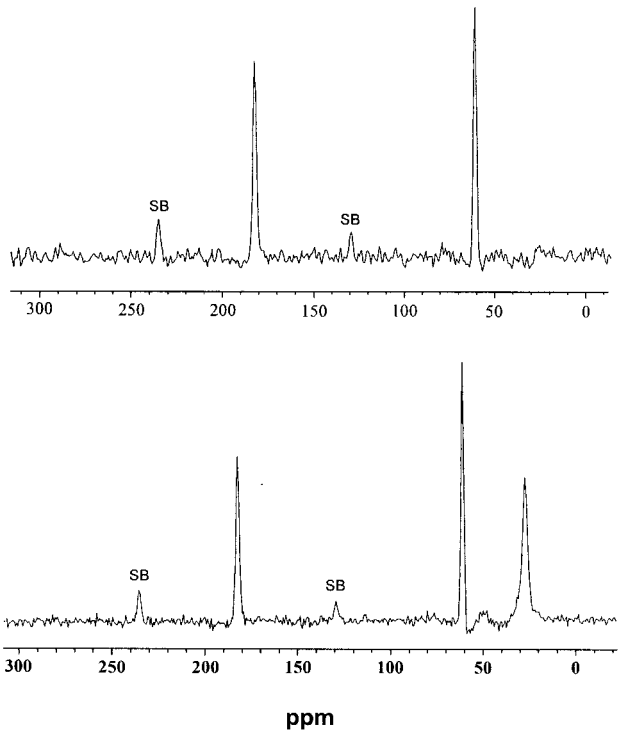


Figure 1. (bottom) Solid-state ^{13}C NMR CP-MAS spectrum of polymer **2** under total suppression of sidebands (TOSS). (top) Solid-state ^{13}C NMR CP-MAS spectrum of polymer **2** under total suppression of sidebands in a gated decoupling experiment.

Structural Characterization of Polymer 2. For reasons that will be discussed in more detail below, hydrolysis of malonate esters $R_2C(COOR')_2$ can also yield a monocarboxylated product, i.e., $R_2CHCOOH$, with loss of one of the two carboxyl groups on the starting substrate.[16−18] Considering that chemistry, the hydrolysis of poly(**1**) could yield either polymer **2** or **3**, depending on whether a decarboxylation occurs subsequently or concomitantly to the hydrolysis (Scheme 1). As a result, efforts were devoted at characterizing the polymer structure, with particular attention being paid on whether a decarboxylation occurred or not. Initial attempts to characterize **2** in solution by NMR spectroscopy failed because of the high ion concentration required to dissolve the hydrolyzed polymer in D_2O, which made it impossible to obtain an acceptable signal-to-noise ratio.

Solid-state ^{13}C NMR experiments were performed under cross-polarization−magic angle spinning (CP-MAS) conditions, using a total suppression of sidebands (TOSS) pulse sequence in order to minimize sidebands.[19] The spectra thus obtained are shown in Figure 1. In the bottom spectrum, three peaks at 28, 62, and 182 ppm can be observed that can be assigned either to the backbone CH_2, $C(COOK)_2$, and COOK carbons of polymer **2** or to the backbone CH_2, $CH(COOK)_2$, and COOK

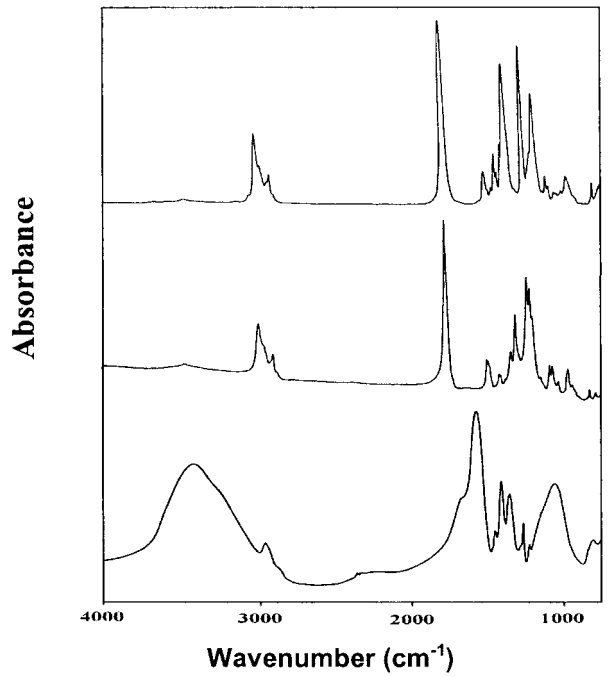


Figure 2. Infrared spectra of monomer **1** (top), poly(**1**) (middle), and polymer **2** (bottom).

carbons of polymer **3**. The absence of signals resulting from residual ester units indicates the efficiency of the hydrolysis. A rapid estimate by a group additivity method of the chemical shifts for the underlined carbons in the hypothetical $RCH_2C(COO^-)_2CH_2CH_2\underline{C}(COO^-)_2$-$CH_2CH_2C(COO^-)_2CH_2R$ and $RCH_2CH(COO^-)CH_2$-$CH_2\underline{C}H(COO^-)CH_2CH_2CH(COO^-)CH_2R$ substructures provided values at 76.1 and 51.6 ppm, respectively.[20] The observed value of 62 ppm lies just in between these two estimates and does not allow to unambiguously distinguish between these two structural possibilities. The chemical shifts observed for the CH_2 and COO^- carbons on the polymers do not allow to discriminate either. A quick test designed at checking the reliability of the COO^- increment provided in the literature demonstrated that chemical shifts could be predicted with an accuracy of ±4 ppm for alkyl-substituted monocarboxylate and malonate ions. This estimate is based on published ^{13}C chemical shift data reported in the literature for carboxylate salts in solution.[21−25] In the investigated polyelectrolytes, electrostatic interactions arising from neighboring carboxylate salts are expected to play a significant, yet difficult to predict, influence on the chemical shifts, which is most probably the origin for the observed discrepancy between theoretical and experimental values.

To unambiguously distinguish between structures **2** and **3**, a gated decoupling solid-state ^{13}C NMR experiment was then performed that allows to selectively observe unprotonated carbons. The obtained spectrum (top spectrum in Figure 1) shows that peaks at 62 and 182 ppm remained unchanged while the peak at 28 ppm disappeared, indicating that the latter peak corresponds to a protonated carbon while the two other signals originate from carbons with no attached hydrogens. This fact can only agree with structure **2** and definitely rules out structure **3** as a possibility.

Infrared spectra of monomer **1** and polymers poly(**1**) and **2** are included in Figure 2. Absorption bands for **2** (bottom spectra in Figure 2) were consistent with the assignment made for potassium malonate in the literature: the strong band at 1573 cm^{-1} was assigned to the stretching vibration in $O{=}C{-}O^-$, and the medium-intensity band at 1676 cm^{-1} and the broad band in the 3000−3700 cm^{-1} region to the in-plane deformation and stretching vibrations of hydration and free water absorbed in the sample, respectively.[26] The strong IR band of the ester carbonyl group that appears at 1734 cm^{-1} in the IR spectrum of the poly(**1**) precursor (middle spectrum in Figure 2) cannot be observed in the IR spectrum of **2**, which again confirms the successful completion of the hydrolysis step.

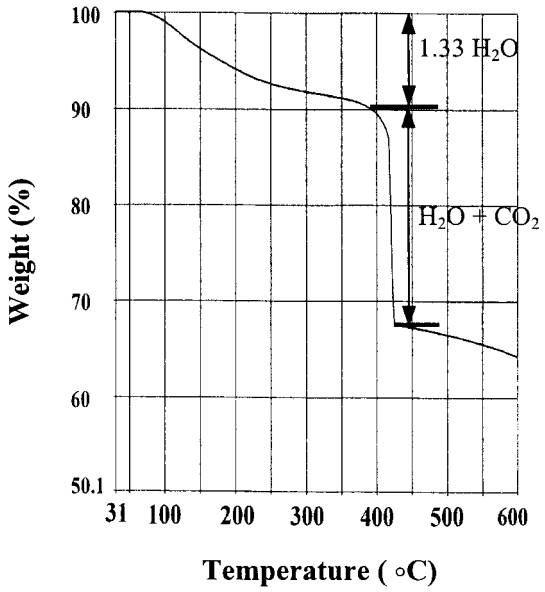
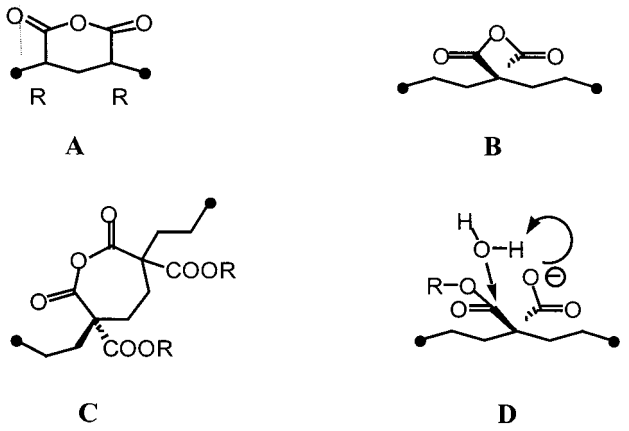


Figure 3. Thermogravimetric curve for polymer **2** (heating rate: 10 K min^{-1}, N_2).

TGA of **2** (Figure 3) indicates that a 10% gradual weight loss occurs from 50 to 400 °C, followed by a sharp 23% weight loss at 400−420 °C and a very slow decomposition at higher temperatures (less than 5% from 420 to 600 °C). It can be hypothesized that the first weight loss is due to the progressive release of water molecules contained in the sample, which includes both physically adsorbed and chemically bound water. Malonate salts like most inorganic compounds are very hygroscopic and can provide hydrates of various stoichiometries.[27−29] Assuming that the macromolecule is entirely dehydrated after the first 10% weight loss, one can calculate that the water content in the starting materials amounts to 1.27 water molecules per malonate repeating unit in the polymer. C−H−K elemental analysis on the other hand indicates that the total amount of water in the polymer sample amounts to 2.33 water molecules for each $CH_2CH_2C(COOK)_2$ unit (based on a very good fit between theoretical composition for $(CH_2CH_2C(COOK)_2{\cdot}2.33\ H_2O)_n$ (C = 24.18%, H = 3.52%, K = 31.49%) and the measured composition (C = 24.21%, H = 2.64%, K = 31.70%)). These results can be reconciled under the hypothesis that the malonate salt is a dihydrate and that the excess physically adsorbed water (0.33 equiv) and the first hydrate water correspond to the first weight loss in the TGA experiment for a total weight loss of 9.7%, which fits very well with the observed 10%. In a second step (23% weight loss at 400−420 °C), one molecule of CO_2 and the second hydrate water are lost simultaneously for a total of 25%, which also compares well with the observed 23%. This assignment is summarized on the thermogram in Figure

Scheme 2



3. The ability for potassium malonate to make a dihydrate has been previously documented in the literature,[27] and thermogravimetric experiments on potassium malonate $K_2C_3H_2O_4$ and its hydrates have indicated that monodecarboxylation occurs around 400 °C as hypothesized here for polymer **2**.[27−29] Both elemental analysis and TGA experiment once again confirm the structure previously assigned for **2**.

Discussion

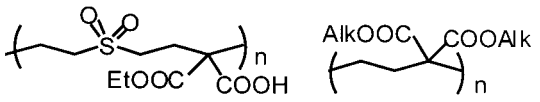
Hydrolysis of ester side substituents located on flexible polymer chains has extensively been studied on acrylate and methacrylate polymers.[30] In general, the hydrolytic reaction can take place under both acidic and basic catalysis, although specific esters generally prefer either one of the two conditions depending on their structures. In some cases the preference is so strong that only one set of conditions can be used in practice. Tertiary esters, for instance, strongly prefer acidic catalysis, while primary esters are often better hydrolyzed under basic conditions. Extensive kinetic studies on the hydrolytic reaction have been carried out under many different sets of experimental conditions and on many different (meth)acrylic polymers. These experiments have led to a few conclusions and structure−reactivity relationships that specifically derive from the polymeric nature of the reagents. A few rules are particularly helpful in rationalizing the sometimes different chemical behaviors observed for polymer-based esters when compared to low molecular weight esters of otherwise similar structures. Under very basic conditions for example, hydrolysis of polyacrylates and polymethacrylates slows down considerably with increasing conversion.[31] This decrease in reactivity can be explained by the progressive appearance of negative charges (carboxylate anions) in the vicinity of the remaining ester groups on the polymer chain. The negative charges of the carboxylate ions introduce a very strong local repulsive interaction toward negatively charged attacking hydroxide ions and efficiently screen adjacent esters from further attack. This makes complete hydrolysis of the polymer under such conditions a very difficult task. When weak bases are used instead or when the concentration of strong bases is maintained sufficiently low, an autoacceleration can be observed, which has been rationalized by the formation of reactive six-membered cyclic anhydrides **A** as intermediates during the reaction (Scheme 2), although general base catalysis by the carboxylate group could be a viable explanation as well.[32,33] The anchimeric assistance provided under these conditions by adjacent carboxylate groups is strongly dependent upon the stereochemical relationship between next neighbors. This, for example, strongly favors the hydrolysis of isotactic PMMA in which optimum orientation of the neighboring esters can be obtained.[31,34] Conversely, hydrolysis of syndiotactic PMMA is very difficult as the formation of the intermediate generates strong transannular interactions between the side substituents of the cyclic intermediate.

Experimental conditions used in this study for the hydrolysis of poly(**1**) were picked up with these observations on the hydrolytic behavior of poly(meth)acrylates in mind. The results obtained during the hydrolysis of poly(**1**), in particular the fact that complete hydrolysis occurs in the presence of potassium hydroxide with no evidence for remaining ester groups, suggests that the reaction does not suffer from the electrostatically driven autoretardation mentioned above. Whether or not neighboring carboxylates provide some anchimeric assistance is not clear and would require some kinetic studies. Given the particular locations of the ester groups on the starting polymer, the cyclic anhydride intermediate would involve either a four- or a seven-membered ring (**B** and **C** in Scheme 2). The highly strained malonic anhydride intermediate **B** can probably be ruled out, its formation being precluded by decarboxylation. A modest intramolecular general base catalysis mechanism has been demonstrated in the hydrolysis of malonate esters via the putative intermediate **D** and might also contribute here.[35] Formation of **C** via the reaction of a carboxylate with an ester group on the next unit is reasonable although slightly less probable than the formation of six-membered intermediate **A**.[36] It must be mentioned, however, that an example has been described in the literature detailing the unexpectedly easy preparation of the seven-membered cyclic anhydride from α,α,α′,α′-tetramethyladipic acid.[37] This ease of formation has been rationalized on the basis of a gem-dialkyl or Thorpe−Ingold effect,[36] although more quantitative data have never been provided. This example is particularly interesting as esters on poly(**1**) are also flanked by quaternary carbons on both side of the succinic unit (**PrOOC**−**C**(R)(COOPr)−**CH$_2$**−**CH$_2$**−**C**(R)(COOPr)−**COOPr**).

It is also interesting to note that no decarboxylation took place during the hydrolysis. Decarboxylation under basic conditions for malonate ester generally occurs at the hemihydrolyzed stage (ROOC−C(R′)$_2$−COO−) where loss of carbon dioxide leads to a carbanion whose electrons can be delocalized on the ester by resonance. At the fully hydrolyzed stage (−OOC−C(R′)$_2$−COO−), decarboxylation is much less favored because of the lower stability of the obtained dianion. (The carboxylate ion is not a good electron-withdrawing group.) This higher stability is reflected in the very high temperature (>350 °C) required to decarboxylate malonate ions (see also the TGA in Figure 3).[27−29] The absence of decarboxylated units in the structure of polymer **2** suggests that decarboxylation of the hemihydrolyzed malonate is also slow in a refluxing water−dioxane mixture. It must be mentioned that malonate-containing polymer **4** was also reported recently to be reluctant to decarboxylate, in agreement with our own findings in this study.[38]

The solubility displayed by **2** in water is extremely and unexpectedly low, the polymer dissolving only in concentrated solution of potassium hydroxide (1 mol

L^{-1}) at temperatures above 80 °C. Aqueous solubility for polyelectrolytes normally increases with the density of ionic groups on the polymers. With two carboxylate groups for two methylene units and one quaternary carbon, **2** has a very high hydrophilic-to-lipophilic balance and should be very soluble as long as the solution is basic enough to prevent protonation and transformation of the carboxylate groups into neutral carboxylic acids. Malonic acid has two pK_a at 2.83 and 5.69, respectively.[39] For reasons similar to those already mentioned above, creation of negative charge at basic pH is expected to progressively prevent further deprotonation and decrease the ionization constants.[40,41] A first explanation for the poor solubility at pH lower than 13 could then be related to an incomplete ionization at these pH.



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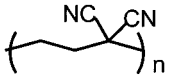

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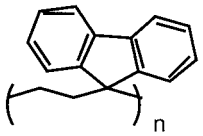

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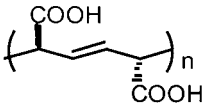

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The very high crystallinity of **2** that results from its high symmetry could be the basis for an alternate explanation. In agreement with the behavior previously observed for polymers with similar architectures, such as poly(dialkyl 1,1-trimethylenedicarboxylate) (**5**),[14,15] poly(1,1-dicyanotrimethylene) (**6**),[42] or poly(fluoren-9,9-diyl-ethylene) (**7**),[43] **2** has a high tendency to crystallize. This behavior results from the high tendency in these systems to adopt a trans conformation for the backbone, which in turn allows to minimize repulsive interactions between substituted quaternary carbons in the chain and side substituents along the chain, and helps to preorganize the chain in the right conformation to crystallize.[44] Evidence that crystallinity is indeed a key factor in the poor solubility of **2** is further supported by a recent paper on another highly charged polyelectrolyte, tritactic poly(muconic acid) (**8**), that was obtained in a very stereoregular form and does not dissolve in water even at very basic pH.[45,46] In this case, the polymer structure is very close to poly(acrylic acid), yet the very high symmetry totally hinders solubilization in water.

Conclusion

The potassium salt of poly(trimethylene-1,1-dicarboxylate) (**2**), a very symmetrical and highly charged anionic polyelectrolyte, can be very easily obtained as a monodisperse polymer by saponification of its ester precursor. The postpolymerization reaction was found to be extremely clean, with no functionalities other than the expected ones identified on the final polymer by several analytical techniques. **2** exhibits interesting physicochemical properties such as a high thermal stability, a low solubility in water, and the potential ability to strongly complex metallic ions via a bidentate malonic ligand. These features suggest that **2** could constitute an interesting template to build nanostructured organic and organometallic ionic solids. Additional experiments are currently under way in order to characterize the key morphological features of the solid and to determine the kinetics of ion exchange under biphasic liquid−solid conditions.

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