Water-Soluble Polymers from Acid-Functionalized Norbornenes

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ABSTRACT: Unprotected *exo,exo*-5-norbornene-2,3-dicarboxylic acid and *exo,exo*-7-oxa-5-norbornene-2,3-dicarboxylic acid were polymerized via ring-opening metathesis polymerization. This reaction yielded polymers with molecular weights (M_n from GPC) ranging from 31 to 242 kg/mol and polydispersity indices between 1.05 and 1.12, using Grubbs' third generation catalyst. The water solubility as a function of pH value of the polymers was investigated by dynamic light scattering (DLS). DLS and acid-base titration revealed that the oxanorbornene polymer was water soluble over a wider pH range than its norbornene analog. © 2009 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 47: 1266–1273, 2009

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INTRODUCTION

Water-soluble polymers are of great interest in many areas of soft materials. On the one hand, they have been used in multiton-scale industrial applications for a long time; on the other hand, they are becoming equally relevant in newly emerging applications such as drug delivery and biomaterials.[1–4] In almost all cases, their water solubility is due to the chemical functionalities on the polymer backbone. We and others have previously reported water-soluble polymers containing noncharged poly(ethylene oxide) (PEO) side chains, as well as positively charged and zwitterionic water-soluble polymers, all of which were obtained by ring-opening metathesis polymerization (ROMP).[5–11] Here, we complement these pre-vious papers with this report on a well-defined polymer obtained from ROMP, which bears two carboxylic acid groups per repeat unit. Water-soluble polymers, mainly with (meth)acrylic backbones, containing the carboxylic acid group are used in waste purification, in the extraction of heavy metals, in paper industry, and as superabsorbers.[12–14] Precise molecular weight and polydispersity control is not crucial for these applications, however for drug delivery, medical applications, and in biological model systems,[15–18] well-defined polymers are required.

We report the synthesis of such defined polymers with narrow polydispersities from the unprotected *exo,exo*-5-norbornene-2,3-dicarboxylic acid, as well as from *exo,exo*-7-oxa-5-norbornene-2,3-dicarboxylic acid, its oxanorbornene analog, by ROMP. Early attempts by Harrison and Feast[19] to polymerize the norbornene dicarboxylic acid monomer (using ROMP with transition metal salts in aqueous media) led to broad polydispersities and yielded only low molecular weights.

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Later, other groups used the popular ruthenium-based catalysis developed by Grubbs to obtain the desired poly(*exo,exo*-5-norbornene-2,3-dicarboxylic acid) or one of its stereoisomers with reasonably narrow polydispersities and good molecular weight control.[11,20,21] However, they were using protection–deprotection chemistry, which added further steps and thus cost to the polymer synthesis. Using the method described here, these polymers can be obtained directly from the unprotected monomer within minutes.

EXPERIMENTAL

Materials

All reagents were obtained from TCI, Sigma-Aldrich, Fluka, or Acros and used without further purification. THF (p.a., Fisher Scientific) was distilled over sodium and benzophenone under nitrogen before use. The third-generation Grubbs' catalyst G3 (dichloro-di(3-bromopyridino)-*N,N'*-dimesitylenoimidazolino-Ru=CHPh) was freshly synthesized as described previously.[22] Titrations were performed using 0.1 M NaOH and 0.1 M HCl standardized solutions from Acros.

Instrumentation

^{1}H NMR and ^{13}C NMR spectra were recorded on a 300-MHz Bruker Spectrospin 300. Gel permeation chromatography (GPC) in THF was performed using a Polymer Laboratories PL-GPC50 instrument with two 5-μm mixed-D columns, a 5-μm guard column, and a Knauer RI detector. The system was calibrated against polystyrene standards, with toluene as the flow marker. Light scattering experiments were performed at room temperature using an ALV unit equipped with an ALV/SP-125 precision goniometer (ALV-Laser Vertriebsgessellschaft m.b.h., Langen, Germany), an Innova 70 argon laser ($\lambda = 514.5$ nm, max. power 3 W, Coherent) operated at 300 mW, and a photomultiplier detector (Thorn EMI Electron Tubes). Signal from the detector was processed by an ALV5000 Multiple Tau Digital Correlator board and associated software. Titrations were performed using a standard glass burette and a Fisher accumet glass electrode.

Monomer Synthesis

Monomer **1a**: (1) The *exo,exo*-5-norbornene-2,3-dicarboxylic anhydride was synthesized according

to the procedure by Lemay and coworkers.[23] (2) 5.00 g (0.030 mol) of *exo,exo*-5-norbornene-2,3-dicarboxylic anhydride was added to 50 mL of water containing 2.00 g (0.035 mol) KOH. The mixture was left for 30 min at room temperature, after which the solution was washed with 500 mL of ethyl acetate. HCl was then added dropwise to the aqueous solution until the diacid precipitated. The colorless solid was dried under vacuum for 24 h, giving 5.4 g (yield 98%) of product.

^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.50$ (d, $J = 1.2$ Hz, 1H, bridge CH_2), 2.18 (d, $J = 1.2$ Hz, 1H, bridge CH_2), 2.70 (s, 2H, CH—COO), 3.15 (s, 2H, bridgehead CH), 6.25 (s, 2H, CH=CH), 9.57 (br s, 1H, COOH); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 180.42$ (COO), 138.05 (CH=CH), 74.86 (bridgehead C), 45.48 (bridge C), 45.35 (C—COO); IR: 935, 1406, 1684, 1684 cm^{-1}; FAB-MS: m/z 183 (M$^+$).

Monomer **1b**: (1) *exo,exo*-7-oxa-5-norbornene-2,3-dicarboxylic anhydride was synthesized according to the procedure published previously.[10] (2) The anhydride thus obtained was reacted with KOH as described earlier for Monomer **1a**.

^{1}H NMR (300 MHz, d_6-DMSO): $\delta = 2.62$ (s, 2H, CH—COO), 5.05 (s, 2H, bridghead H), 6.44 (s, 2H, CH=CH), 12.18 (COOH). ^{13}C NMR (75 MHz, d_6-DMSO): $\delta = 172.48$ (COO), 136.25 (CH=CH), 79.50 (bridgehead C), 45.91, (C—COO).

Homopolymer Synthesis

Grubbs' third-generation catalyst G3 was synthesized according to the literature.[22] Both polymers **2a** and **2b** were obtained using the same method. The polymerization was performed under strict exclusion of oxygen. The appropriate amounts of each reagent are given in Table 1. In a typical experiment, 0.10 g (0.55 mmol) of diacid monomer **1a** and 1.3 mg (5.9 μmol) 2,6-di-*tert*-butyl-4-methylphenol (BHT) were placed in a Schlenk flask and evacuated for 10 min. An appropriate amount of G3, depending on desired MW, was placed in another Schlenk flask and evacuated for 10 min. Freshly distilled THF was placed in a third Schlenk flask and degassed by three freeze-pump-thaw cycles. One milliliter of this solvent was added to both monomer and catalyst. The monomer solution was then added to the stirred catalyst solution and quenched after 4 min with 0.5 mL of ethyl vinyl ether. The polymer was recovered by precipitation from ether as a colorless solid. Details on the polymer characterization by GPC are given in Table 2.

Table 1. Polymerization Parameters and Characterization Results for Polymers **2a** and **2b**

Polymer	Monomer (mmol)	Initiator (μmol)	$M_{n,Target}$ (kg/mol)	$M_{n,GPC}$ (kg/mol)	M_w/M_n
2b	1.30	1.25	192	242	1.09
2b	1.30	2.40	100	136	1.06
2a	1.50	1.50	182	140	1.12
2a	1.50	3.00	91	86	1.05
2a	0.36	1.10	60	76	1.07
2a	0.18	1.80	18	49	1.05
2a	0.22	1.70	24	31	1.09

Polymer **2a**: [^1]H NMR (300 MHz, CDCl$_3$): $\delta =$ 1.19 (br s, 1H, bridge CH_2), 1.99 (br s, 1H, bridge CH_2), 2.75 (s, 2H, CH—COO), 3.20 (br m, 2H, CH=CH—CH, cis and trans), 5.24 (s, 1H, C=CH, cis), 5.43 (s, 1H, C=CH, trans), 12.03 (br s, 2H, COOH). Polymer **2b**: [^1]H NMR (300 MHz, d_8-THF): $\delta =$ 3.00 (s, 2H, CH—COO), 4.49 (br s, 1H, CH=CH—CH, trans), 4.92 (br s, 1H, CH=CH—CH, cis), 5.51 (s, 1H, C=CH, cis), 5.76 (s, 1H, C=CH, trans), 12.57 (br s, 2H, COOH).

Polymer Derivatization for GPC Analysis

The polymer (20 mg) was dissolved in methanol/THF (1:1). Two milliliters of trimethylsilyldiazomethane (2 M solution in hexanes) were added to the solution. After 15 min, the solvent and the excess reagent were removed under vacuum, and then the samples were analyzed by GPC.

Sample Preparation for Dynamic Light Scattering

The samples were dried overnight in a vacuum oven, massed out and allowed to stir over night in about 10% of the solvent volume that was to be added. After adding the remaining solvent, they were heated to about 50 °C for 1 h, ultrasonified for 5 min, and filtered with 0.45-μm Millipore filters.

RESULTS AND DISCUSSION

The synthesis of the target polymers, poly(*exo, exo*-5-norbornene-2,3-dicarboxylic acid) and its oxanorbornene analog poly(*exo,exo*-7-oxa-5-

Table 2. Dynamic Light Scattering Results for Polymers **2a** and **2b**: Hydrodynamic Radii of Single Chains (S) and Aggregates (A), (a) for Different Solvent Systems at pH $\sim$ 7, and (b) Different pH Values

		(a) R_h (nm)							
		THF		0.01 M NaCl		0.1 M LiBr		H$_2$O	
Polymer	$M_{n,target}$ (kg/mol)	S	A	S	A	S	A	S	A
2a	182	8.8	–	8.0	111	7.5	101	2.3	95
2b	100	9.5	–	10.3	58	12.6	69	n.d.	n.d.
2b	192	13	–	14.2	185	16.1	170	10.1	151

		(b) R_h (nm)									
		pH = 3		pH = 5		pH = 7		pH = 9		pH = 11	
Polymer	$M_{n,target}$ (kg/mol)	S	A	S	A	S	A	S	A	S	A
2a	182	6.9	109	8.7	93	13.6	124	16.0	152	16.3	120
2b	100	9.9	117	17.0	180	16.2	Large	15.7	122	16.9	259
2b	192	7.7	86	21.1	150	22.1	Large	21.9	178	22.4	173
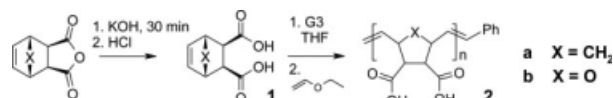
Scheme 1. Synthesis and polymerization of the diacid monomers **1a** and **1b**.

norbornene-2,3-dicarboxylic acid), is shown in Scheme 1.

We have previously experienced difficulties when polymerizing acid-containing monomers by ROMP and found that the polymerization only worked well when the acid groups were fully protonated, as carboxylate anions would act as a ligand to the ruthenium catalyst and thereby quench or retard the polymerization.[8,24] As a result, special care was taken in the monomer syntheses to obtain the bis-protonated carboxylic acids. Monomer purity was checked by NMR [Fig. 1(a), shown for monomer **1a**], and the broad peak from 9 to 10 ppm indicated that the diacid was obtained. Additionally, the monomers were titrated with NaOH to determine the number of acidic protons. As expected, 100% protonation was obtained (Fig. 4, see discussion later).

The polymerization was conducted in nonaqueous media (THF) because the third-generation Grubbs catalyst is insoluble in water. Using NMR to monitor the reaction, complete monomer conversion was observed within minutes. As a small higher molecular weight peak was found in the gel permeation chromatogram of initial polymerization attempts, a radical scavenger (BHT) was

added to the polymerization mixture. Using BHT, the higher molecular weight peak disappeared, suggesting that it was caused by a side reaction involving radical formation.

The polymers thus obtained were analyzed by NMR and GPC (in THF using polystyrene standards). To avoid analytical complications such as enthalpy interactions of the charged, polar sample with the nonpolar GPC column, the samples for GPC analysis were methylated using trimethylsilyl diazomethane. A representative GPC curve is shown in Figure 2. The GPC peak is narrow and symmetrical; only for the higher molecular weight samples, a slight tailing on the low-molecular flank was observed. The GPC results for polymers **2a** and **2b** are summarized in Table 1. All polydispersities were below 1.12, indicating good reaction control.

The ^{1}H NMR spectrum for polymer **2a** is shown in Figure 1(b). The peak corresponding to the monomer's double bond at 6.25 ppm has vanished, and a new group of peaks for the double bond protons (cis and trans isomers) in the polymer at 5.0 to 5.7 ppm appeared. Likewise, the peak at 6.44 in Monomer **1b** was replaced by two peaks at 5.51 and 5.76 ppm in Polymer **2b** (spectra not shown).

When the polymer samples were mixed with water, after an initial swelling period, clear solutions were obtained upon stirring overnight. However, such a solution might still contain aggregates that would appear transparent to the eye. To check for aggregation, dynamic light scattering experiments were performed on selected samples
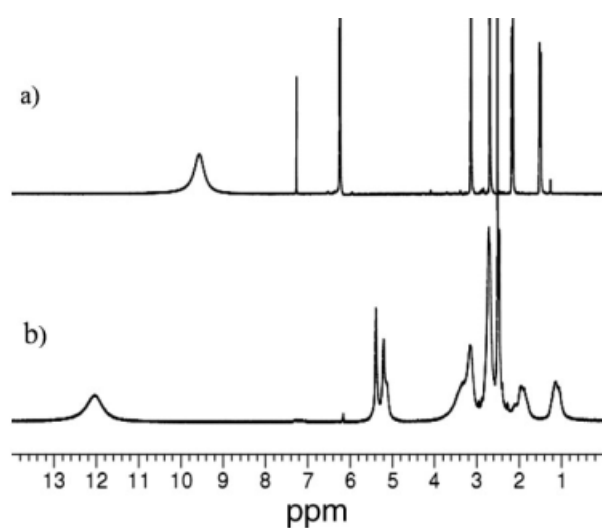
Figure 1. ^{1}H NMR spectra of Monomer **1a** (CDCl$_3$/top) and Polymer **2a** (THF-d_8/bottom). See Experimental section for peak assignment.
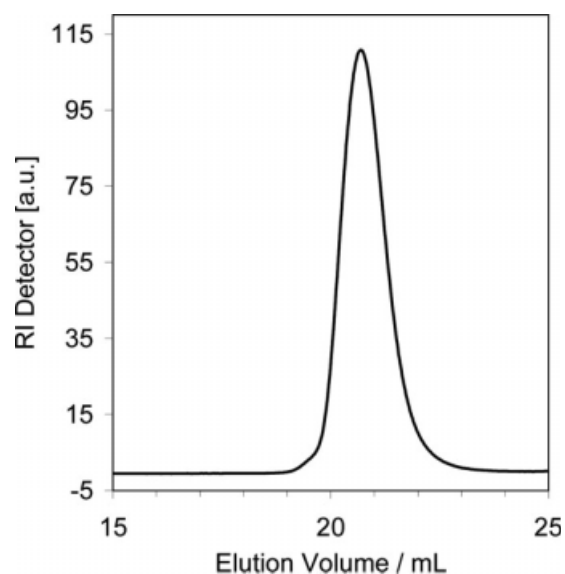
Figure 2. GPC curve for Polymer **2a** (THF, polystyrene standards).

of both polymers **2a** and **2b**. The solution concentration was 1 g/L and the scattering angle (θ) was varied from 30° to 120°. Extrapolation of $\theta \to 0$ gave the apparent hydrodynamic radius, which is the hydrodynamic radius at that concentration. A representative electric field correlation function $g^2(t)$ is shown in Figure 3(a), along with a plot of the intensity-weighted relaxation time distribution at $\theta = 30°$ for that sample (Polymer **2b**, 100 kg/mol, 0.1 M LiBr). The correlation function indicates that two diffusive processes are present, most likely corresponding to the diffusion of single polymer chains and aggregates. These two processes appear as two distinct peaks in the intensity-weighted relaxation time distribution [Fig. 3(a)]. Since the measurements were taken at high salt concentrations, the second diffusive process cannot be attributed to the usual "slow mode" observed for polyelectrolytes.[25] After transforming the relaxation time distribution into a mass-weighted hydrodynamic radii distribution [Fig. 3(b)], the areas under each peak could be used to estimate the mass percentage of aggregates versus free chains in the sample. The mass percentage was about 25%, meaning that a significant amount of the sample is aggregated. The dynamic light scattering results for the same sample in THF are shown in Figure 3(c,d). This data shows that aggregation is insignificant in the organic solvent. These light scattering experiments were repeated with a variety of additives in an attempt to find an aqueous system without the high-molecular weight aggregates. For all samples investigated, aggregates were observed, even at high salt concentrations. Both the amount of aggregation as well as the aggregate dimensions varied with the exact sample preparation conditions (stirring, heating, and ultrasonification conditions). Typical aggregate sizes are given in Table 2. In contrast, all samples were soluble as single chains in THF. Since the backbone of the polymer is hydrophobic, it is assumed that the backbones of these polymers aggregate[*] avoid contact with the hydrophilic solvent despite the two carboxylic acid groups per repeat unit.

It was further found that the level of coil expansion of these polymers is pH dependent, as illustrated in Figure 3(e). For the two samples of Polymer **2b**, the hydrodynamic radius is approximately constant from pH 5 to 11. The chains shrink significantly at pH 3, and the polymer precipitates upon further pH reduction. For Polymer

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[*]In aqueous media.

2a, the range of solubility is even lower, as the chains continuously shrink with lower pH from an initial hydrodynamic radius of 16 nm at pH 11 and 9, until they precipitate below pH 3. This behavior is consistent with the expectation that by decreasing the pH, the degree of protonation of the polymer is increased, and thus its negative charge decreases. By leaving less and less carboxylate groups on the polymer backbone, the water solubility is eventually lost. Polymer **2b** has an oxygen atom instead of a CH_2 group in its backbone, which makes it more hydrophilic than polymer **2a**. This functional group seems to be involved in solubilizing the polymer in water through hydrogen bonding. Therefore, the polymer chain of polymer **2b** has the same size from pH 5 to 11, whereas the chain of its CH_2 analog **2a** starts to shrink already at pH 7 to avoid polymer–solvent contacts.

This trend is the opposite of what was found previously published for polymers with poly(norbornene) and poly(oxonorbornene) backbones, respectively, which were substituted with PEO side chains.[7] Counterintuitively, some aggregation was found for these oxanorbornene-based polymers, yet the norbornene-based ones were dissolved as single chains. Although the PEO side chain length was the same for the two polymers, their molecular weight and thus the number of repeat units of the backbone was different (57 kg/mol for the norbornene vs. 90 kg/mol for the oxanorbornene).[7] Therefore, it seems more likely, in the light of these results for Polymers **2a** and **2b**, that the molecular weight difference of the previously reported polymers was responsible for the differences in aggregation behavior and not the chemical difference of their backbones.

To better understand the correlation between pH value and solubility, as detected by DLS, the Polymers **2a** and **2b** were titrated with NaOH. The titration curves for the 100 and 91 kg/mol samples of Polymers **2a** and **2b** are shown in Figure 4 as pH versus theoretical degree of neutralization, which is the percentage of base added as compared with the theoretical number of protons in the titrated sample aliquot.

(Degree of neutralization

$$= \frac{n_{OH} \cdot 100}{n_{acid}} = \frac{2 \cdot C_{OH} \cdot V_{OH}}{\frac{m_{sample}}{M_{sample}}},$$

where n is the number of moles, c the concentration in mol/L, V the volume, m the mass, and M the molecular weight of the repeat unit.) As discussed earlier, full protonation was found when
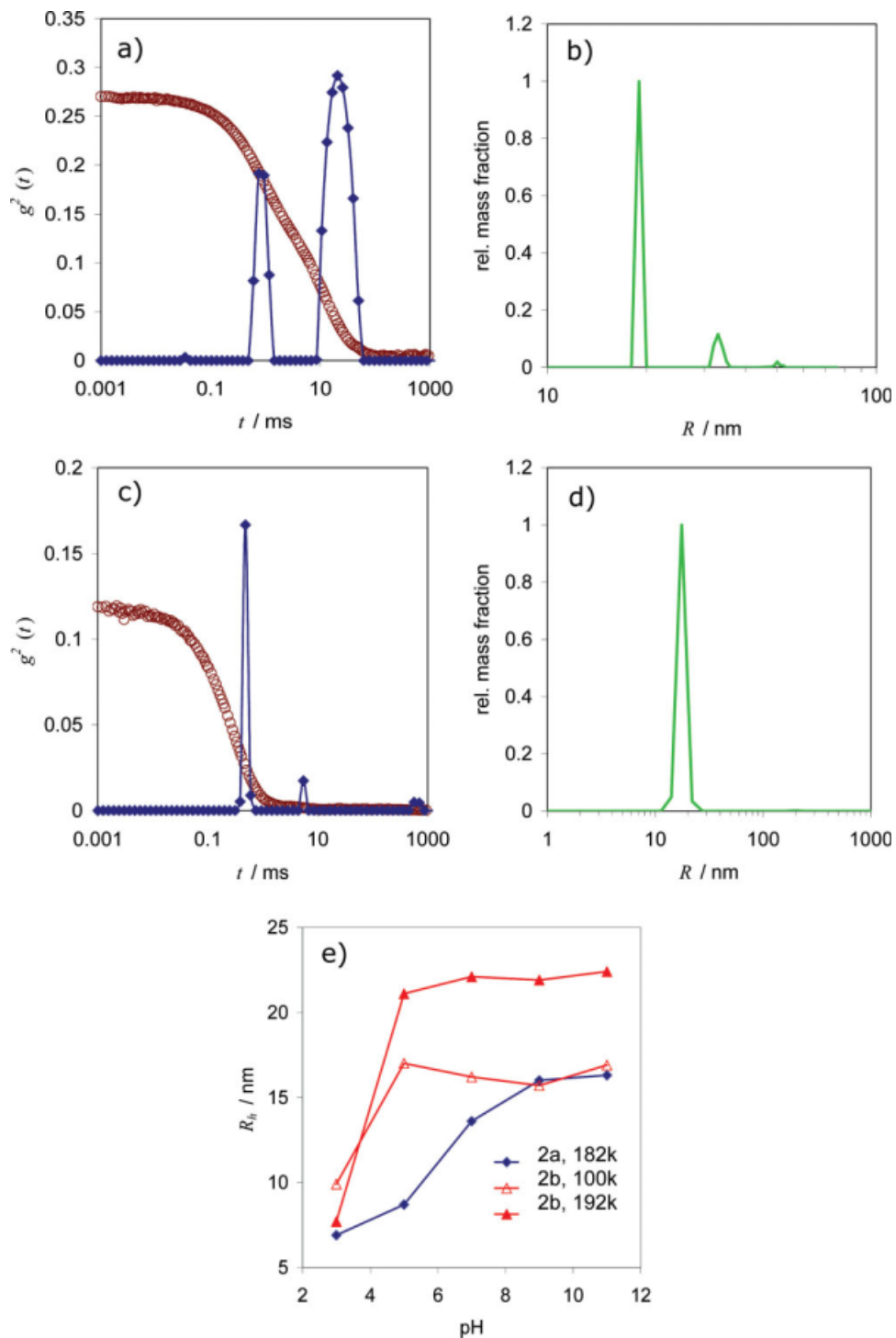
Figure 3. Dynamic light scattering results for Polymer **2b**, M_n = 100 kg/mol, at θ = 30 °C: electric field correlation function (red) and intensity-weighted relaxation time distribution function (blue) (a) in 0.1 M aqueous LiBr solution, and (c) in THF; mass-weighted radius distribution function (b) in 0.1 M aqueous LiBr solution, (d) in THF; (e) hydrodynamic radii of the single chains as a function of pH. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
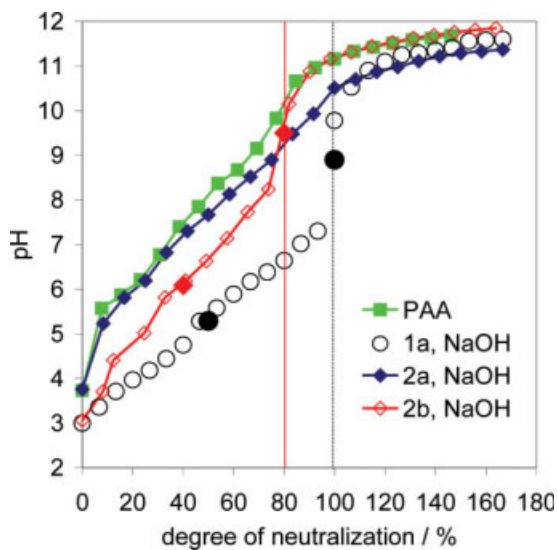
Figure 4. Titration curve for Monomer **1a**, Polymers **2a** (91 kg/mol) and **2b** (100 kg/mol), and poly(acrylic acid).

Monomer **1a** was titrated. The equivalence point and the half-equivalence point for that monomer are each marked with a black solid dot in Figure 4. The equivalence point and half-equivalence point for Polymer **2b** are marked with a red solid diamond. Unlike the monomer, which could be titrated to 100%, only 80% of the calculated amount of carboxylic acid groups was found for Polymer **2b**, despite careful sample purification and drying. For Polymer **2a**, the titration curve is much shallower around the equivalence point than that of Polymer **2b**, and the exact location of that point is therefore somewhat ambiguous; although it seems to be also located in the 80–85% region. The titration curve of commercially available poly(acrylic acid) (PAA) is given in the same figure for comparison. For this polymer, only 85% of the calculated amount of carboxylic acid groups was found, which is in line with the results from the ROMP polymers. The shape of the titration curve of PAA is very similar to that of our polymers. Literature reports that the pKa value of acrylic acid is 4.25, while that of poly(acrylic acid) is 6.8.[26] From the titration curves, a pKa value (which is the pH at the half-equivalence point) for Monomer **1a** of 5.3 was determined. Because the titration curve shape of PAA and that of Polymer **2a** is almost identical up to about 60% of neutralization, the pKa of Polymer **2a** has to be similar to that of PAA. The trend toward higher pKa values for Polymer **2a** as compared with its monomer is in line with the literature data.[26] The pKa value of Polymer **2b** was found to be 6.1.

Shapes of polyelectrolyte titration curves are nontrivial and depend on a variety of parameters, such as the polyelectrolyte concentration, the ionic strength, and the chemical nature of the polyelectrolyte itself, as is discussed in the polyelectrolyte literature.[27,28] Without going into numerical details of the theory, the difference in solubility, as evidenced by DLS, of our two polymers can still be rationalized qualitatively. The titration curve of Polymer **2b** is always below that of **2a** up to approximately the equivalence point, where the curves intersect. This means that Polymer **2b** is more acidic, presumably due to the inductive effect of the oxygen. Therefore, at a given pH, Polymer **2b** has more charged carboxylate groups than Polymer **2a**, which increases its solubility. This is in agreement with the DLS data, which shows that Polymer **2b** is soluble over a wider pH range than Polymer **2a**.

CONCLUSION

In this report, we have demonstrated that monomers bearing unprotected carboxylic acid groups can be polymerized via ROMP using Grubbs' third-generation catalyst. The polymers thus obtained had narrow polydispersities from 1.05 to 1.12 over a molecular weight range from 31 to 242 kg/mol. It was demonstrated that good reaction control was achieved. Although they dissolve to give optically clear solutions in water, it was shown that a significant amount of aggregates is present in aqueous solutions from these polymers, regardless of the salt additive or pH of the solvent. Although the aggregation is undesirable for specialty applications such as drug delivery, as these polymers can be obtained in a single synthetic step from the (homemade or commercially obtained) monomer, they are attractive building blocks for soft materials applications where aggregation is not a problem. Postpolymerization backbone modification to increase the hydrophilicity of the polymer might eventually reduce or even prevent the aggregation.

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