

Fluorine-free, methacrylate-based compleximer materials with an accessible glass transition

by

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Abstract

Due to the reversible nature of the ionic bond, materials based on ionic interactions are a promising alternative to plastics with covalent crosslinking. The mechanical properties of such polyelectrolyte complex materials (PECs) are typically highly dependent on plasticization by water and salt, as they are brittle and unprocessable when dry. In compleximers, a variation on a PEC material, plasticization is achieved intrinsically by including bulky hydrophobic tails on the charged monomers to moderate the ionic interactions. Compleximers are processable in dry state, recyclable, and insensitive to water and solvents, but they still require additional plasticization by ionic liquids to control the glass transition and rely on hydrophobic fluorinated side groups to screen the charges. Here, a new compleximer material is prepared from methacrylate-based polyelectrolytes with bulky hydrocarbon side-chains. These methacrylate-based compleximers are easily processable under mild conditions, recyclable by hot-pressing without loss of mechanical properties, and have an accessible glass transition in the absence of external plasticization. The hydrocarbon side-groups are a more sustainable alternative to the fluorinated tails and sufficiently weaken the ionic interactions, while maintaining reasonable water and solvent resistance. Thus, by changing the polymer backbone and side-chain chemistry the compleximers' material properties can be optimized.

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1. Introduction

In the ongoing efforts to develop more sustainable plastics, one of the challenges is to find a recyclable alternative to chemically crosslinked plastics, while maintaining their material properties, such as mechanical strength and chemical resistance.¹ While various dynamic covalent chemistries have been developed as a more reversible alternative to traditional covalent crosslinks, they are often difficult to synthesize and cannot easily be tuned.² Non-covalent strategies include supramolecular interactions, which are dynamic and reversible in nature and allow macromolecules to assemble into materials with a wide variety of properties.³ Among these are materials based on ionic interactions, of which polyelectrolyte complexes (PECs) in particular have been studied extensively.⁴ PECs are formed when oppositely charged polymers are combined in solution, where they separate into a dense phase as a result of electrostatic attraction between the charged units and an entropy gain upon release of the counterions.^{5,6} Depending on the hydration level and ionic strength, PECs can be liquid-like coacervates or solid precipitates.^{7,8} In the presence of water they can be processed into dense materials, which are also known as saloplastics.⁹ While these materials have shown useful properties, they require plasticization by water,¹⁰⁻¹² as well as salt,^{13,14} to screen the charges and weaken the ionic interactions. In absence of plasticizers, the strong electrostatic forces within the complexes result in a glass transition temperature that lies above the material's thermal degradation point and cannot be reached.^{15,16} In consequence, PECs are brittle and impossible to process in their dry state,¹⁴ thus limiting their application as plastics.

Recently, Van Lange et al.¹⁷ have developed a new variation on a polyelectrolyte complex material which circumvents the dependence on external plasticization by water and salt. In these complexes, called 'compleximers', plasticization is achieved intrinsically by including bulky hydrophobic tails on the charged monomers to moderate the electrostatic forces. Van Lange et al.¹⁷ show that the internal screening of the charges in compleximers results in a material that is processable and recyclable, as well as solvent- and water resistant, thus combining thermoplasticity with thermoset characteristics. However, the compleximers still required additional plasticization by ionic liquids to control the glass transition and improve the toughness of the material. Moreover, the styrene-based polyanions that were used rely on fluorinated side-groups to screen the charges and reduce water sensitivity, which limits the sustainability of the material as perfluoroalkyl substances are typically harmful and difficult to degrade.¹⁸

In this work, a compleximer material is prepared from polyelectrolytes with a different chemical structure (Figure 1), with the aim to optimize the compleximers' material properties. The styrene-backbone of the original design is replaced by a methacrylate-backbone to enhance the processability of the compleximer, as this improves the solubility of the polymers, as well as influences the compleximer's glass transition temperature. In addition, the fluorinated tails of the polyanion, which were inspired by ionic liquids, are exchanged for bulky hydrocarbon groups as a more sustainable alternative. The effects of the changes to the polymer structure on the compleximers' processability, thermomechanical properties and water and solvent resistance are investigated.

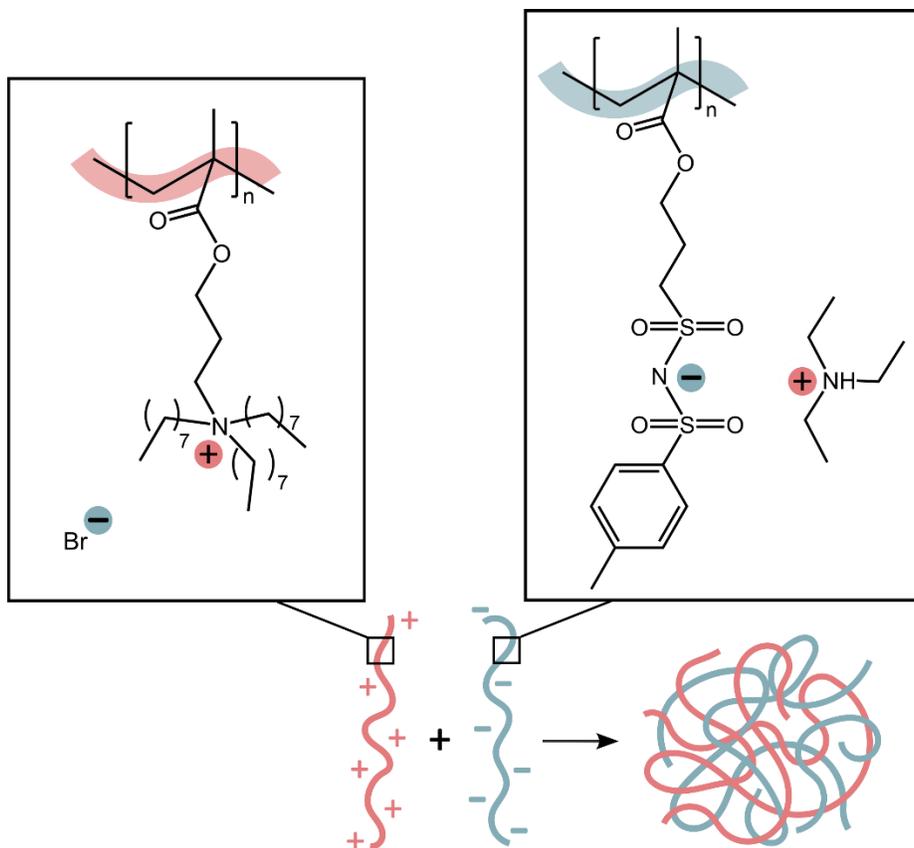


Figure 1: Fluorine-free, methacrylate-based polyelectrolytes and compleximer. Chemical structures of the polycation (left) and polyanion (right), including a schematic representation of the formation of the compleximer. The counterions, bromide ions and triethylamine, are washed out after complexation.

2. Materials and Methods

2.1 Materials used for synthesis

Trioctylamine (98%), 3-Bromopropan-1-ol (97%), Triethylamine ($\geq 99\%$), Methacryloyl chloride ($\geq 97\%$), 3-Sulfopropyl methacrylate potassium salt (98%), p-Toluenesulfonamide (98%), 4-Methoxyphenol (99%), Sodium bicarbonate (NaHCO_3), Magnesium sulfate (MgSO_4 , anhydrous), Azobis(2-methylpropionitrile) (AIBN, 98%), Ammonium persulfate (APS, $\geq 98\%$), Dichloromethane (DCM, anhydrous), Tetrahydrofuran (THF, anhydrous) and Dimethylformamide (DMF, anhydrous) were obtained from Merck. Oxalyl chloride ($>98\%$) was purchased from TCI. Deuterated solvents were bought from Buchem. All other solvents were obtained from Biosolve.

2.2 Polymer synthesis

2.2.1 Synthesis of polycation

The synthetic procedure for the cationic polymer was adapted from Wrede et al. (2012).¹⁹

Synthesis of 3-hydroxypropyl trioctylammonium bromide (HPTOAB)

Trioctylamine (6.36 g, 18.0 mmol) was added to a flask and degassed for 30 min with nitrogen before adding 3-bromo-1-propanol (10.0 g, 72.0 mmol) and degassing again for 10 min. The mixture was stirred at 60 °C for 2 days. The product was precipitated in 250 mL diethyl ether. The precipitate was filtered and dried under vacuum at 40 °C overnight, yielding a white powder (6.49 g, 13.2 mmol, 73%).

Synthesis of 3-(methacryloyloxy)propyl trioctylammonium bromide (MAPTOAB)

HPTOAB (2.50 g, 5.07 mmol) was dissolved in 30 mL anhydrous DCM and degassed with nitrogen for 10 min before adding triethylamine (2.06 g, 20.3 mmol). The solution was cooled to 0 °C and degassed again for 30 min, followed by the stepwise addition of methacryloyl chloride (1.60 g, 15.2 mmol). The reaction mixture was stirred overnight. The excess methacryloyl chloride was quenched by adding 100 mL of a saturated aqueous NaHCO_3 solution to the obtained suspension, resulting in phase separation. The organic phase was washed 4 times with 20 mL of saturated NaHCO_3 solution and dried over MgSO_4 . The solvent was removed under vacuum at 25 °C, yielding a yellow oil (2.17 g, 3.87 mmol, 76%).

Synthesis of poly(3-(methacryloyloxy)propyl trioctylammonium bromide) (pMAPTOAB)

MAPTOAB (2.97 g, 5.30 mmol) was dissolved in 30 mL anhydrous THF. The solution was degassed with nitrogen for 20 min and heated to 60 °C, before AIBN (8.69 mg, 0.0530 mmol) was added. The solution was degassed with nitrogen again for 10 min and then stirred at 60 °C overnight. The reaction mixture was concentrated under vacuum before precipitating in a cold mixture of 1:2 THF/H₂O. The precipitate was dried under vacuum at 60 °C overnight, yielding a yellow, sticky polymer (1.33 g, 45%), which was stored in a desiccator.

2.2.2 Synthesis of polyanion

The synthetic procedure for the anionic polymer was adapted from Kammakakam et al. (2020).²⁰

Synthesis of 3-(chlorosulfonyl)propyl methacrylate (SPMA-Cl)

3-Sulfopropyl methacrylate potassium salt (30.0 g, 122 mmol) was dissolved in about 50 mL anhydrous THF. The solution was degassed with nitrogen for 30 min and cooled to 0 °C before adding 3.4 mL of anhydrous DMF as a catalyst. The solution was degassed again, followed by the dropwise addition of oxalyl chloride (25.0 g, 197 mmol). The reaction mixture was stirred at 0 °C for 1 hour, then left stirring at room temperature overnight. Ice was added to the obtained suspension to quench the excess oxalyl chloride, resulting in phase separation. After decanting the upper aqueous layer, the organic layer was diluted with 160 mL DCM. The organic solution was washed 6 times with 35 mL water, then dried over MgSO₄. The solvent was removed under vacuum at 25 °C, yielding a light-yellow oil (18.3 g, 80.5 mmol, 66%).

Synthesis of triethylammonium 1-[3-(methacryloyloxy)propylsulfonyl]-(p-toluenesulfonyl)imide (MATSI)

p-Toluenesulfonamide (13.8 g, 80.5 mmol) was dissolved in 50 mL anhydrous THF and degassed with nitrogen for 30 min. The solution was cooled to 0 °C, before triethylamine (17.9 g, 177 mmol) was added and the solution was degassed again. SPMA-Cl (18.3 g, 80.5 mmol) was dissolved in 30 mL anhydrous THF, degassed with nitrogen for 20 min and added to the reaction mixture. The reaction was stirred at 0 °C for 1 hour, then left stirring at room temperature overnight. The resulting suspension was filtered. A catalytic amount of 4-methoxyphenol was added to the filtrate as inhibitor, before concentrating the solution under vacuum at 25 °C. The product was dissolved in 175 mL DCM. The solution was washed 3 times with 50 mL water. The remaining aqueous phases were extracted with ethyl acetate. Solvents were removed under vacuum at 25 °C, resulting in a yellow oil (9.57 g, 20.7 mmol, 26%).

Synthesis of poly(triethylammonium 1-[3-(methacryloyloxy)propylsulfonyl]-(p-toluenesulfonyl)imide) (pMATSI)

MATSI (2.25 g, 4.86 mmol) was dissolved in 25 mL water. The solution was degassed with nitrogen for 20 min and heated to 60 °C, followed by the addition of APS (11.1 mg, 0.0482 mmol). The solution was degassed again for 10 min and then stirred at 60 °C overnight. The solvent was removed under vacuum. The product was dissolved in 6 mL dimethyl sulfoxide (DMSO) before precipitating in cold ethyl acetate. The precipitate was dried under vacuum at 60 °C overnight, yielding a yellow, sticky polymer (1.96 g, 87%), which was stored in a desiccator.

2.3 Compleximer formation

To form the compleximers, the polycation (1.09 g) and polyanion (0.90 g) were each dissolved in a 1:1 mixture of acetonitrile/water at 0.125 M. The solutions were mixed in equimolar amounts and stirred overnight at room temperature. The resulting suspension was filtered. The precipitate was resuspended in MilliQ water to wash out the small counterions by stirring vigorously. The water was replaced twice per day, which has been shown to remove counterions effectively,¹⁷ until the ionic conductivity of the supernatant reached equilibrium near the conductivity of MilliQ water (Figure A3). The complex was isolated by filtration and dried in a vacuum oven at 60 °C overnight to obtain a white powder (1.40 g, 85%), which was stored in a desiccator.

The conductivity of the supernatants from each compleximer washing cycle was measured using a Knick 703 conductometer equipped with a 2-electrode probe with a cell constant of 1.08 cm⁻¹.

2.4 Material processing

Hot-pressing

The compleximer powder was hot pressed in a Specac manual hydraulic press equipped with heated platens to create circular or rectangular samples using pressing dies obtained from Zhengzhou TCH Instrument Co.

0.10 g or 0.13 g of compleximer powder was added to a circular pressing die (10 mm) or a rectangular pressing die (20 x 5 mm), respectively. The die was preheated for 15 minutes at 120 °C, before a pressure of 1.5 tons was applied for 15 minutes. After releasing the pressure, the die was removed from the press and cooled down for at least 30 minutes before the sample was removed.

Recycling

Hot-pressed samples were ground into a coarse powder using a Blaupunkt FCG701 coffee grinder. A finer powder was obtained by subsequent grinding in a 20 mL IKA ball milling tube using the IKA ULTRA-

TURRAX® Tube Drive with 15 stainless steel for 3 minutes at power level 9. The powder was hot-pressed again as described.

2.5 Analytical methods

Nuclear magnetic resonance spectroscopy (NMR)

¹H-NMR spectra were recorded on a Bruker AV400 MHz spectrometer using CDCl₃ or D₂O as solvent. The spectra and chemical shifts are given in Appendix A.

Static light scattering (SLS)

The molecular weight of the polymers was estimated by static light scattering measurements performed on an ALV instrument equipped with a 660 nm laser. Three runs of 20 s were performed at every detection angle over a range from 30 to 130° in intervals of 2°. Analysis details and results are described in Appendix B.

Thermogravimetric analysis (TGA)

The thermal stability of the individual polymers and compleximer was determined using a PerkinElmer STA 6000. Approximately 5 mg of sample was added to a ceramic sample cup and weighed. The sample was heated under an air flow of 20 mL/min at a rate of 10 °C/min from 30 to 600 °C and upon reaching 600 °C kept isothermal for 5 minutes.

For the isothermal measurement, the sample was kept isothermal for 30 minutes at 120 °C, 140 °C and 160 °C consecutively to simulate degradation during material processing and mechanical testing.

X-ray photoelectron spectroscopy (XPS)

The elemental composition of a hot-pressed compleximer sample was determined using a JEOL JPS-9200 photoelectron spectrometer. Monochromatic Al K α X-ray radiation was applied at 12 kV and 20 mA with an analyzer energy pass of 10 eV for narrow scans. The spectra were processed using the peak fitting program in CasaXPS software.

Dynamic mechanical analysis (DMA)

The mechanical properties of the compleximer were analyzed using an Anton Paar 702 Space Multidrive. A DMA fixture was used for extensional oscillatory measurements on rectangular compleximer samples. Temperature ramps were performed for temperatures between 25 °C and 100 °C by applying a heating ramp followed by a cooling ramp (3 °C/min), while oscillating with a 0.01% strain at a frequency of 1 Hz

and with a preload force of 1500 Pa. Amplitude sweeps were performed at room temperature at a frequency of 1 Hz for strains between 0.001% and 0.01%, which are in the linear viscoelastic regime of the material.

Additionally, a 10 mm plate-plate geometry with a crosshatched surface on the upper plate was used for measurements in oscillatory shear mode on circular samples. Amplitude sweeps were performed at room temperature at a frequency of 1 Hz to determine the linear viscoelastic regime of the material. Temperature ramps were performed for temperatures from 90 °C up to 140 °C or 180 °C by applying a heating ramp followed by a cooling ramp (3 °C/min) while oscillating with a 0.01% strain at a frequency of 1 Hz and with a preload force of 2 N. Measurements were repeated twice in a row to ensure good contact between the sample and the plate. The shear moduli were converted to extensional moduli by multiplying by 3 (assuming Poisson's ratio to be 0.5). A small difference remains between the shear and extensional data, due to different samples and ways of measuring.

3. Results and Discussion

3.1 Stable, processable compleximers are formed under mild conditions

Compleximers are formed by dissolving each of the oppositely charged polyelectrolytes in a common solvent before mixing them to acquire the compleximer as a precipitate. For the original compleximer design, this complexation was only possible in a mixture of DMF and toluene at low concentrations (0.055 M) and under extensive heating, as the styrene-based polyelectrolytes were difficult to dissolve.¹⁷ The replacement of the hydrophobic fluorinated tails and the styrene-backbone has resulted in a notable improvement in the solubility of the methacrylate-based polyelectrolytes. Whereas the polycation readily dissolves in common organic solvents such as ACN, THF and DMF, the polyanion is water-soluble. This facilitated the complex formation process considerably, as both polymers could be easily dissolved in a mixture of ACN and water at a concentration of 0.125 M. This not only reduced the used amount of organic solvents, but the process also did not require any heating, and ACN and water are easier to remove from the product than DMF and toluene. The compleximer was obtained as a dry powder, which could be transformed into cohesive samples by hot-pressing at 120 °C (Figure 2a). As normal PECs are impossible to process in absence of water and salt,^{10,15–17,21,22} the ability to be hot-pressed in dry state confirms that the ionic interactions within the complex are sufficiently weakened to generate thermoplasticity. Moreover, it shows that this effect can be achieved by hydrocarbon side-groups, and does not require hydrophobic fluorinated side-chains.

The minimum processing temperature and time required to successfully hot-press the material were the same as what Van Lange et al.¹⁷ found for their compleximer. Whereas they observed slight porosity in their hot-pressed material, the resulting samples here were transparent, indicating that the structure of the hot-pressed complex is very dense and contains few or no pores. Thermogravimetric analysis (TGA) also shows that the complex has improved thermal stability compared to the individual polyelectrolytes (Figure 2b and Figure A4a). The compleximer appears to be stable up to about 200 °C, although a slight decrease in weight (<2%) is observed from about 145 °C, which could be a small impurity. This is still well above the processing temperature. Extended heating at the processing temperature also does not result in material degradation, as shown in an isothermal TGA measurement (Figure A4b). Thus, the compleximer does not degrade during processing.

Elemental analysis by x-ray photoelectron spectroscopy (XPS) proves that the ratio between the polycation and polyanion within the compleximer is stoichiometric (Figure 2c, d). However, the XPS spectra also show the presence of neutral nitrogen atoms in addition to the positively charged and negatively charged nitrogen atoms, which was not expected. No major impurities are visible in the monomer and polymer NMR spectra (Figure A1). The compleximer was thoroughly washed and dried after complexation. TGA shows no traces of evaporation of volatile solvents, and based on conductivity measurements of the supernatants, all counterions were assumed to be removed during washing (Figure A3). Nevertheless, a fraction of triethylamine could be deprotonated and in consequence not completely washed out. As the polycation and polyanion are still present in equal amounts, and the impurity is not charged, its effect on the compleximer's properties is assumed to be limited.

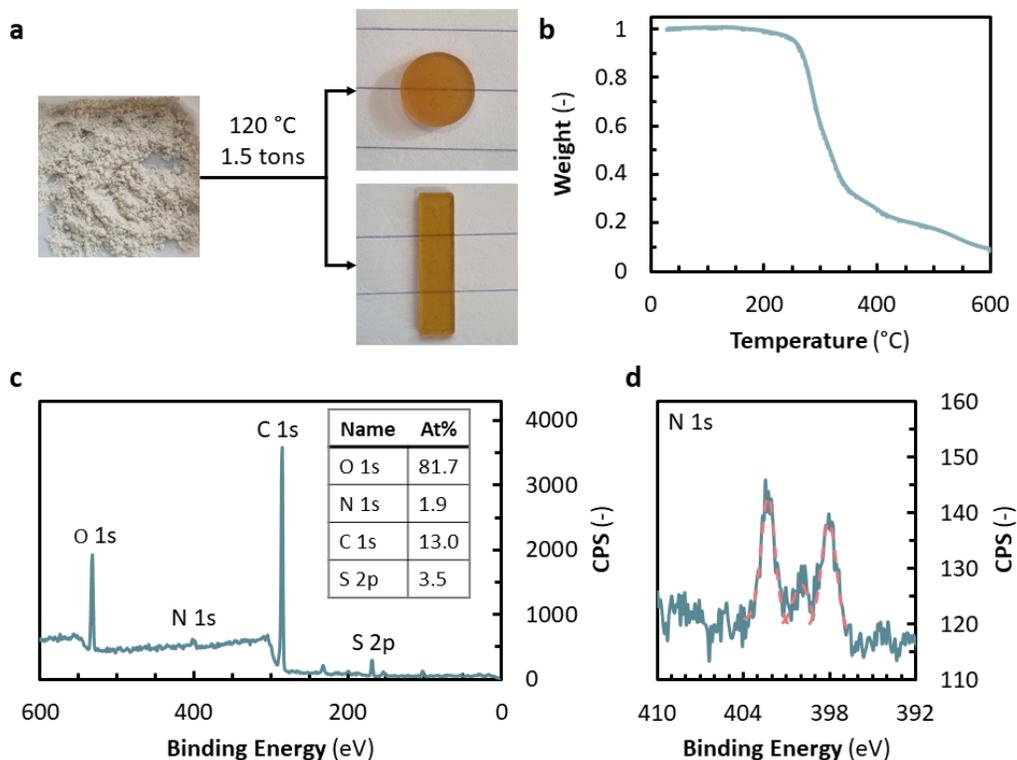


Figure 2: Processability, thermal stability and elemental composition of the compleximer. a) Dry compleximer powder can be hot-pressed in cohesive, transparent samples. b) Thermal stability of the compleximer, as measured by TGA. The compleximer is stable up to about 200 °C, which is well above the processing temperature. c) Wide XPS spectrum of the compleximer. The atomic percentages shown in the inset correspond reasonably well to the expected ratios. d) Narrow scan of the nitrogen (N 1s) region, showing three signals with slightly shifted electron binding energies corresponding to positively charged (left), negatively charged (right) and neutral (middle) nitrogen atoms. The ratio between N^+ and N^- is about 42%:40%, confirming that the compleximers have formed approximately stoichiometrically. The neutral nitrogen atoms correspond to about 18%. The fitted peaks are plotted as red dashed lines.

3.2 The glass transition is reached without external plasticization

In traditional PECs, thermal transitions have only been observed in hydrated state.^{9,10,16,23} Due to the strong ionic interactions in dehydrated PECs, they do not experience glass transitions below their decomposition temperature. Van Lange et al.¹⁷ showed that the ionic interactions in their compleximer were sufficiently weakened to allow the material to soften with increasing temperature, but they did not observe a glass transition until the material was further plasticized by adding ionic liquid. The thermomechanical properties of the methacrylate-based compleximer material were characterized by dynamic mechanical analysis (DMA) in temperature ramps with an oscillatory strain in extensional and shear mode (Figure 3a, b). The storage modulus, which represents the elastic response of the material, is higher than what was reported for the styrene-based compleximers,¹⁷ indicating an increased stiffness. Moreover, the storage modulus was found to decrease with increasing temperature, which indicates that the material softens, and suggests the presence of a glass to rubber transition. Indeed, at about 140 °C the compleximer reaches

a glass transition temperature (T_g), here defined as a peak in the loss tangent ($\tan \delta$), which is the ratio between the loss modulus and storage modulus. The T_g lies below the decomposition temperature measured by TGA, which has not been reported before in dry, unplasticized PEC materials. The decreased T_g in the methacrylate-based compleximer implies an improved material processability and toughness. Which change in the polymer structure is mainly responsible for the improved thermomechanical properties compared to the original compleximers remains unknown. The polymer backbone is known to affect T_g , but the side-groups have also been replaced, which weaken the ionic interactions and thus also affect thermal transitions. In addition, the polymers were likely shorter than the styrene-based polyelectrolytes used by Van Lange et al.¹⁷ (Appendix B), which can also contribute to lowering the T_g .

Interestingly, upon increasing the temperature beyond the T_g , $\tan \delta$ decreases only slightly (Figure 3c, d), while in traditional thermoplastics typically a sharp peak is observed. Increasing the temperature even further leads to an increase in $\tan \delta$ again. This phenomenon was also observed in ionomers, polyelectrolytes in which only part of the monomers are charged, and suggests the presence of multiple relaxation modes,^{24–26} although the exact mechanisms remain unknown. Repeating the measurement causes a shift in the modulus and $\tan \delta$ with each cycle, and a color change from yellow to brown was observed in the sample. This suggests that the structural rearrangement is at least partly irreversible, or that some degradation may have occurred. Up to the glass transition this effect is not observed.

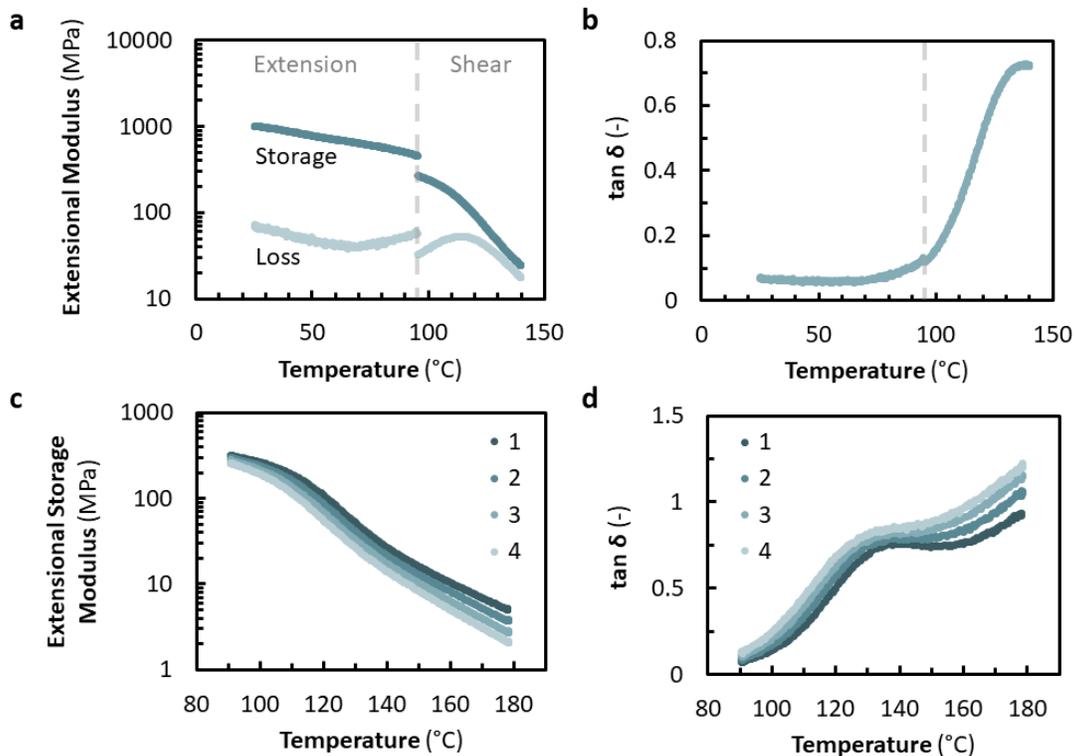


Figure 3: Thermomechanical behavior of the compleximer. Changes in a) extensioal storage and loss moduli and b) $\tan \delta$ as a function of temperature, characteristic for a glass transition. Above 95°C the measurements were performed in shear mode instead of extensional, as indicated by the gray dashed lines. Shear moduli were converted to extensioal moduli. Graphs are averages of three samples each. Heating beyond T_g results in changes in c) extensioal storage modulus and d) $\tan \delta$ over multiple cycles.

3.3 Thermoplastic and thermoset characteristics are retained

Although the compleximer material is glassy and brittle at room temperature, the presence of a glass transition indicates the compleximer is malleable when heat is applied. Indeed, under gentle heating by a heat gun the material softens and can be easily bended without breaking (Figure 4a). The compleximer material is thus easily processable. Likewise, the compleximer can be recycled by grinding and re-processing the material. After multiple cycles, the storage modulus and $\tan \delta$ remain unaffected (Figure 4b). This means the thermoplastic characteristics of compleximers as reported for the original styrene-based compleximer¹⁷ have been retained in the methacrylate-based compleximer.

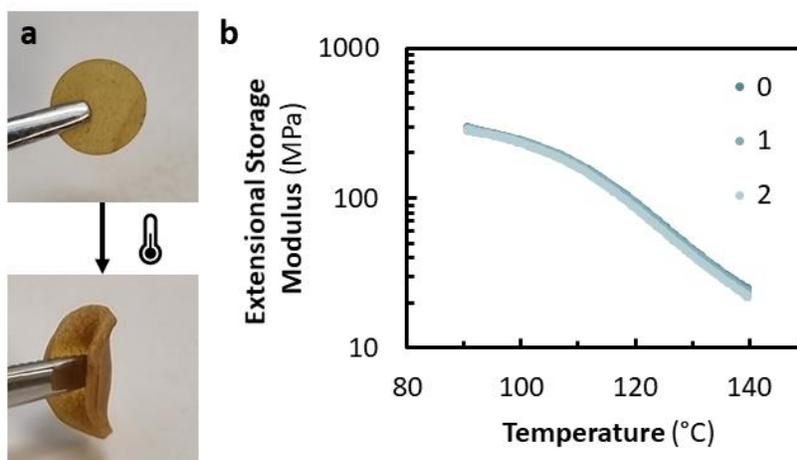


Figure 4: Malleability and recyclability of the compleximer. a) The compleximer can be reshaped without breaking upon gentle heating with a heat gun. b) The thermomechanical properties of compleximer samples are unaffected by multiple cycles of grinding and re-processing.

The styrene-based compleximers were also reported to have thermoset characteristics.¹⁷ Whereas PECs are known to exhibit a significant loss of mechanical performance upon immersion in water,^{17,27} and typically swell or dissolve completely at high ionic strength,^{8,14,28} the styrene-based compleximers were resistant to water and salt, as well as common organic solvents.¹⁷ However, it was hypothesized that the fluorinated tails played a large role in the compleximers' hydrophobicity,¹⁷ which suggests that the lack of fluorinated side-groups in the new design may affect the material's water and solvent resistance. Indeed, after 24 hours of immersion in water, the storage modulus of the methacrylate-based compleximer is reduced to about half of its original value (Figure 5a), confirming that the compleximer is not completely insensitive to water. However, the storage modulus does not continue to decrease, as the value is approximately the same after a week of immersion. The storage modulus after immersion is also still within the same order of magnitude as the modulus of dry compleximer, whereas traditional PECs exhibit a loss of mechanical properties over several orders of magnitude upon immersion in water.¹⁷ In addition, no dissolution or swelling is observed after four weeks of immersion in a solution of 2.5 M KCl (Figure 5c, i), and in a range of common organic solvents (Figure 5d-g, j-m). Yet, in ACN and DMF the compleximer pieces have turned white and opaque, suggesting the material has become more porous, while in the

styrene-based compleximer only swelling was observed in DMF and toluene.¹⁷ Thus, the material is not as insensitive to water and a few common organic solvents as the original styrene-based compleximer. Nevertheless, the methacryate-based compleximer does not dissolve or swell upon contact with water, salt or solvents, therefore retaining a reasonable level of resistance even without the hydrophobic, fluorinated tails.

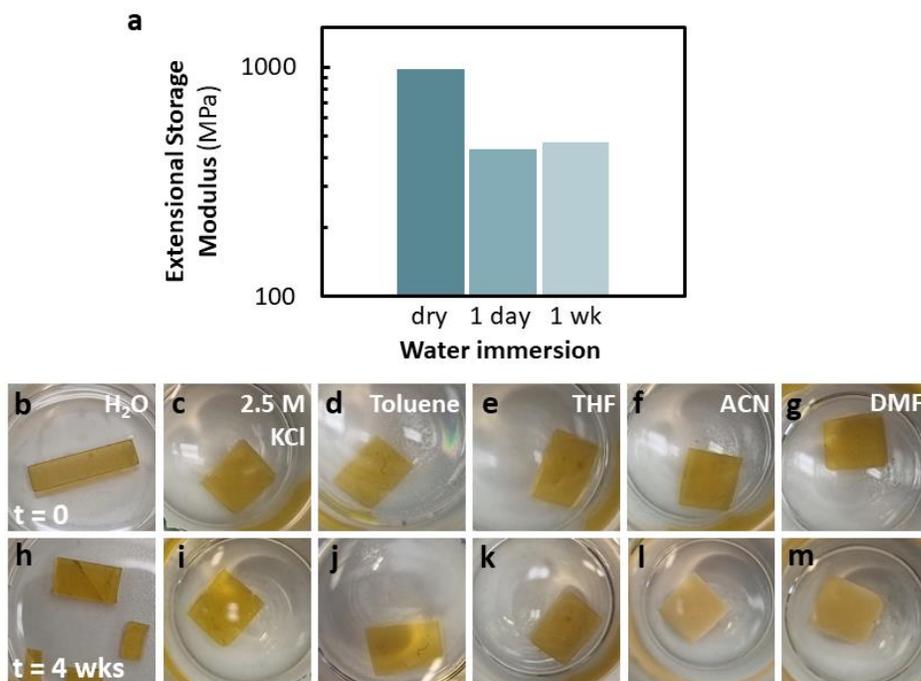


Figure 5: Water, salt and solvent resistance of the compleximer. a) The storage modulus of the compleximer is reduced by immersion in water overnight but remains stable after a week of immersion. Compleximer samples directly after immersion in b) water, c) 2.5 M KCl in water, d) toluene, e) THF, f) ACN and g) DMF. After four weeks of immersion the compleximer samples in h) water, i) 2.5 M KCl, j) toluene and k) THF have not visibly changed. The sample in water was broken during a DMA measurement. Samples in l) ACN and m) DMF have turned white and opaque.

4. Conclusion and Outlook

This work shows that compleximers can be formed from methacrylate-based polyelectrolytes, in which bulky hydrocarbon side-groups sufficiently weaken the ionic interactions to create an easily processable, recyclable material with an accessible glass transition without the need for external plasticization. The methacrylate-based compleximer is not as completely insensitive to water and solvents as the original compleximer design, but maintains reasonable resistance, and the removal of the fluorinated side-chains from the polymer structure enhances the potential of the compleximer as a sustainable plastic. Thus, by changing the backbone and departing from the initial ionic liquid-inspired side-chain chemistry the compleximers' properties have been further optimized.

Further analysis may be useful to gain additional insight in the compleximer's mechanical properties. Since the storage modulus of the compleximer decreases upon immersion in water, the question arises how the mechanical properties are affected by air humidity. Moreover, stress-strain tests are needed to determine the compleximer's mechanical strength. Stress relaxation tests can also contribute to elucidating the relaxation mechanisms that occur above the glass transition, such as whether the compleximers exhibit vitrimer-like behavior and undergo bond-exchange reactions at high temperatures.

To further optimize the mechanical properties, more variations of the polymer structures can be explored. Although the methacrylate-based compleximer has an accessible T_g , at room temperature the material still behaves glassy and is relatively brittle. Hence, further reduction of the T_g is required to create a tough, elastomeric compleximer. This may be achieved by replacing the methacrylate-backbone of the polymers by an acrylate-backbone, which has a lower intrinsic T_g . Investigating compleximers with a lower charge density on the polymers to decrease the number of ionic interactions can also contribute to softening the material, although a too low charge density may affect the compleximer formation and the material's strength. Lastly, other fluorine-free side-chain chemistries can be explored for the polyanion to fine-tune the balance between easy processability and hydrophobicity, which affects both the level of charge screening and water resistance. This will help to fully realize the potential of the compleximers as a recyclable alternative to covalently crosslinked plastics.

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Appendices

Appendix A: $^1\text{H-NMR}$ results of the synthesized polymers

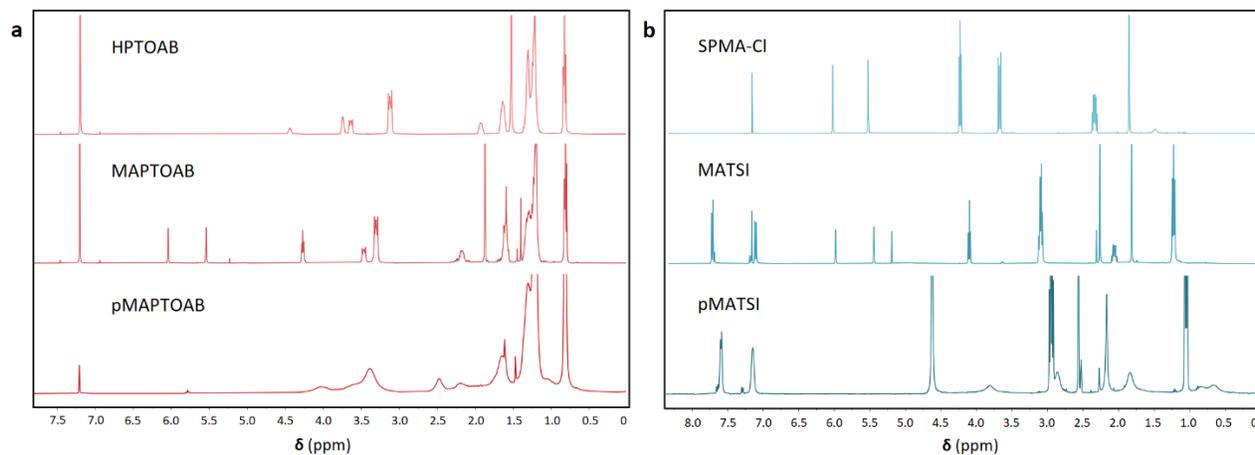


Figure A1: $^1\text{H-NMR}$ spectra of all synthesized compounds. Spectra of synthesized intermediate, monomer and polymer of a) the polycation synthesis and b) the polyanion synthesis. The spectrum of pMATSI was recorded in D_2O . All other spectra were recorded in CDCl_3 .

Table A1: $^1\text{H-NMR}$ results of all synthesized compounds. Chemical shifts for the synthesized polycation and polyanion, including intermediates and monomers.

Compound	Solvent	$^1\text{H-NMR}$ (400 MHz, δ ppm)
HPTOAB	CDCl_3	4.43 ppm (broad, 1H), 3.74 ppm (t, 2H), 3.63 ppm (t, 2H), 3.11 ppm (t, 6H), 1.92 ppm (m, 2H), 1.65 ppm (m, 6H), 1.29 ppm (m, 12H), 1.21 ppm (m, 18H), 0.82 ppm (t, 9H)
MAPTOAB	CDCl_3	6.04 ppm (s, 1H), 5.54 ppm (s, 1H), 4.27 ppm (t, 2H), 3.47 ppm (t, 6H), 2.19 ppm (m, 2H), 1.87 ppm (s, 3H), 1.59 ppm (m, 6H), 1.22 ppm (m, 30H) 0.81 ppm (t, 9H)
pMAPTOAB	CDCl_3	3.82-4.35 ppm (2H, broad), 2.91-3.82 ppm (6H, broad) 2.33-2.73 ppm (2H, broad), 2.01-2.33 ppm (3H, broad), 1.50-2.01 ppm (6H, broad), 0.93-1.50 ppm (30H, broad), 0.68-0.93 ppm (9H, broad)
SPMA-Cl	CDCl_3	6.06 ppm (s, 1H), 5.56 ppm (s, 1H), 4.27 ppm (t, 2H), 3.71 ppm (t, 2H), 2.38 ppm (m, 2H), 1.89 ppm (s, 3H)
MATSI	CDCl_3	7.74 ppm (d, 2H), 7.15 ppm (d, 2H), 6.02 ppm (s, 1H), 5.49 ppm (s, 1H), 4.13 ppm (t, 2H), 3.15 ppm (m, 8H), 2.30 ppm (s, 3H), 2.10 ppm (m, 2H), 1.85 ppm (s, 3H), 1.27 ppm (t, 9H)
pMATSI	D_2O	7.45-7.68 ppm (2H, broad), 6.99-7.23 ppm (2H, broad), 3.52-4.12 ppm (2H, broad), 2.93 ppm (m, 6H), 2.64-2.89 ppm (2H, broad), 2.03-2.24 ppm (3H, broad), 1.56-2.02 ppm (3H, broad), 1.04 ppm (t, 9H), 0.43-0.93 ppm (2H, broad)

Appendix B: Polymer weight estimation by static light scattering

To estimate the molecular weight of the polyelectrolytes from the obtained scattering intensities, the Rayleigh ratio R was calculated for each detection angle θ using

$$R(\theta) = \frac{I_{sample}(\theta) - I_0(\theta)}{I_{ref}(\theta)} R_{ref} \left(\frac{n_0}{n_{ref}} \right)^2 \quad (1)$$

where $I_{sample}(\theta)$, $I_0(\theta)$, and $I_{ref}(\theta)$ are the scattering intensities of the sample, solvent and reference, respectively, n_0 and n_{ref} are the refractive indices of the solvent and reference, respectively, and R_{ref} is the Rayleigh ratio of the reference. The polycation was dissolved in THF with $n_0 = 1.409$, and the polyanion was dissolved in water with $n_0 = 1.332$. Toluene was used as a reference with $n_{ref} = 1.494$ and $R_{ref} = 8.56 \times 10^{-4} \text{ m}^{-1}$.²⁹ The Rayleigh ratio was plotted against scattering angle $q = (4\pi n_0/\lambda) \sin(\theta/2)$ with λ the wavelength of the laser (Figure A2). The relation between the Rayleigh ratio and molar mass is given by

$$R_\theta = K_R C M_w \quad (2)$$

in dilute samples. Here C is the mass concentration, M_w is the molar mass of the polymer, and K_R is an optical constant given by

$$K_R = \frac{4\pi^2 n_0^2 (dn/dC)^2}{\lambda^4 N_{av}} \quad (3)$$

in which N_{av} is Avogadro's number, and dn/dC is the specific refractive index increment of the polymer. dn/dC was assumed to be 0.15 mL g^{-1} for both polyelectrolytes, as this is usually between 0.14 and 0.16 mL g^{-1} for polymers. R_θ is found by extrapolating R to a zero detection angle, after which the molecular weight follows from $M_w = \frac{R_\theta}{K_R C}$.

The resulting molecular weights (Table A2) suggest the methacrylate-based polyelectrolytes are shorter than the styrene-based polymers used by Van Lange et al.¹⁷ However, the obtained molecular weights may deviate if the real dn/dC values are significantly different from the value that was estimated. For a more accurate determination of the polymer weight the polymers' dn/dC values need to be determined experimentally. Moreover, the polymers are polydisperse, which results in an overestimation of the polymer weight, as the larger molecules scatter more in SLS. An alternative analysis technique would be to use a gel permeation chromatography method where the charges of the polyelectrolytes are neutralized to prevent interactions with the column.

Table A2: Molecular weight of the synthesized polymers. Polymer weight for the polycation and polyanion as estimated by SLS.

Polymer	Solvent	Molecular weight (g mol^{-1})
pMAPTOAB	THF	$4.3 \times 10^5 \text{ g mol}^{-1}$
pMATSI	Water	$4.1 \times 10^4 \text{ g mol}^{-1}$

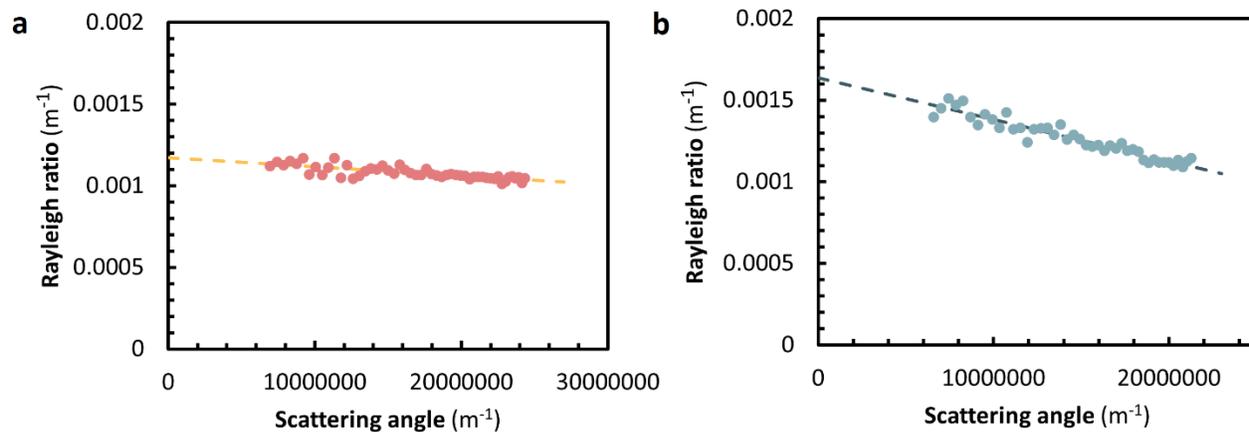


Figure A2: Static light scattering results of the synthesized polymers. Rayleigh scattering ratio for each scattering angle of a) polycation and b) polyanion. The extrapolation to a zero detection angle is shown as a dashed line.

Appendix C: Conductivity and thermal stability during processing

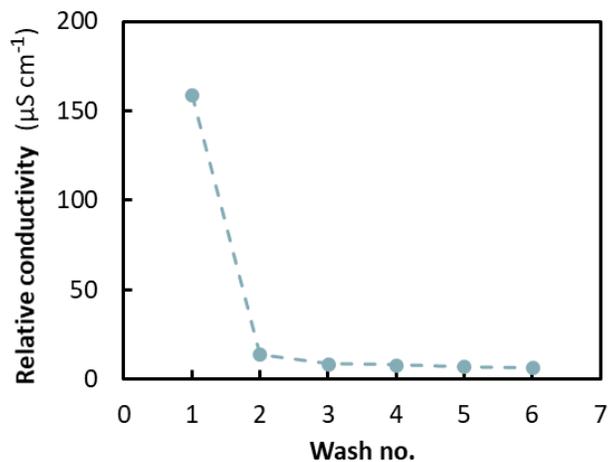


Figure A3: Washing of the compleximer. The conductivity of the supernatant phases of each compleximer washing cycle relative to MilliQ water. The counterions released upon complexation are washed out.

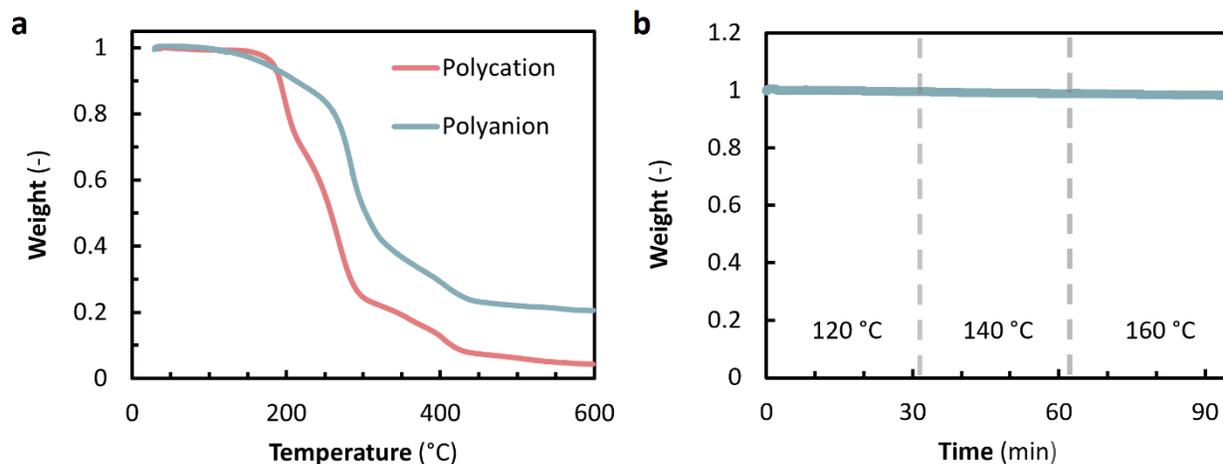


Figure A4: Thermal stability of the individual polyelectrolytes and the compleximer during processing. a) Thermal stability of the polycation and polyanion, as measured by TGA. The polyelectrolytes have a lower decomposition temperature than the compleximer. b) Thermal stability of the compleximer at processing and measurement temperatures, as measured by isothermal TGA. The slight reduction in weight (<2%) occurs at a constant rate at each temperature and is likely due to baseline drift of the measuring instrument.