Poleable Nanoparticles as Fillers Towards Non-linear Optically Active Actuators

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ABSTRACT

A new type of poleable dielectric elastomer is introduced herein. The elastomer contains polymer nanoparticles with frozen molecular dipoles, which can be oriented at elevated temperatures in an electric field *via* poling. The aim is to provide a soft material with high, tunable optical properties suitable for actuator and flexible electronics applications. To that end poleable polymeric nanoparticles with high dipole concentrations and glass transition temperatures well above room temperature will be needed to be used as filler in an elastomer matrix. The synthesis and characterization of such particles is presented in this manuscript. Polyhydroxyethyl methacrylate (PHEMA) nanoparticles were synthesized using miniemulsion polymerization. The particles were loaded with 4-[ethyl (2-hydroxyethyl) amino]-4-nitrobenzene, usually called Disperse Red 1 (DR1), which has a large dipole moment ($\mu = 7.5 - 9.5$ D).¹ The maximum dipole loadings is limited by the solubility of the dipole in the monomer solutions prior to polymerization. All samples show a glass transition temperature around 95 °C. Secondary electron microscopy (SEM) revealed spherical particles, the size of which was confirmed by dynamic light scattering (DLS) measurements. A composite was prepared by dispersing the particles in polydimethyl siloxane (PDMS).

Keywords: poling, dipole, PHEMA, DR1, miniemulsion polymerization, polymeric nanoparticles, permittivity, PHEMA-co-DR1.

1. INTRODUCTION

Dielectric elastomer actuators (DEAs) are a new type of electromechanical transducers based on the ability of an elastic capacitor to change dimensions when an electric field is applied.^{2,3,4} Linear actuators with output properties similar to that of biological muscle could have an immense impact in areas such as industrial and personal robotics, orthopaedic assists and medical devices in general.³ DEAs consist of an elastic film sandwiched between two compliant electrodes.⁵ When an electric voltage is applied, positive and negative charges are transferred onto the electrode surfaces inducing an electrostatic pressure which compresses and elongates the film, converting electrical energy into mechanical work. The

electrostatic pressure (p) acting on the film and the strain in thickness (s_z) direction are given by:^{2c} $p = \epsilon \epsilon_0 \left(\frac{U}{d} \right)^2$ and s_z

$= \frac{p}{K}$, where ϵ is the relative permittivity of the film, ϵ_0 the permittivity of free space, U the applied voltage, d the thickness of the film and K the compression modulus. In contrast to traditional ceramic linear actuators, DEAs show a number of advantages: they are cheap, easy to process, lightweight, flexible and show actuation displacements on a macroscopic scale.⁶ The main reason preventing the widespread use of DEAs is the high electric field necessary to achieve reasonable actuation.⁷ The most common solution to this problem is to increase the relative permittivity of the material by blending it with highly polarizable fillers.^{8,9,10} Although ϵ can be significantly increased at concentrations approaching the percolation threshold, dielectric losses increase due to agglomerations and conducting pathways.¹¹

The poling of polymers containing dipolar molecules is a well-established method to create polar non-centrosymmetric materials and is frequently used for non-linear optical (NLO) materials.^{12,13,14} The alignment of the dipole in an amorphous polymer is done in a high electric field at temperatures above its glass transition temperature (T_g) followed by freezing of the oriented material by cooling below T_g while the electric field is maintained. The oriented dipoles lead to, among other properties, higher ϵ .

Poleable fillers are a necessary first step towards this goal. They can be realized by synthesizing the particles directly using emulsion polymerization.^{15,16} The feasibility of the method is explored by synthesizing dipoles containing PHEMA particles using miniemulsion polymerization and characterizing their morphology and dielectric response. DR1 and its methacrylate functionalized version (DR1MA) are the most frequently studied dipoles in NLO, and were chosen for this study (Figure 1).

Figure 1. Chemical structure of DR1 and DR1MA.

2. EXPERIMENTAL PART

2.1 Materials

All chemicals were purchased from Aldrich and used as received, except when noted otherwise. The hydroxyl end-terminated PDMS AB116665 ($M_w=139'000$ g/mol) and the (25-35% methylhydrosiloxane)-dimethylsiloxane-copolymer AB109380 crosslinker (XL) were purchased from ABCR. Solvents were purified and dried by standard procedures. Poly(ethylene-*co*-butylene)-block-poly(ethylene oxide) surfactant¹⁷ and DR1MA were synthesized according to literature.¹⁸

2.2 Characterization

¹H NMR spectra were recorded on a Bruker Avance-400 spectrometer (400 MHz at room temperature). Gel permeation chromatography (GPC) measurements in tetrahydrofuran (THF) eluent were done with an Agilent 1100/PSS WinGPC 8.1 system calibrated with polymethylmethacrylate standards (Polymer Standards Service). Two columns (100, 1000 Å pore size SDV-Gel) and a flow rate of 1 ml min⁻¹ were used. Signals were detected with a UV and RI detector. GPC measurements with dimethylformamide (DMF) as eluent were done on a GPCv2000 from Waters using a solution of 0.1% LiCl in DMF at a flow rate of 0.6 ml min⁻¹ at 60 °C, three columns (Styragel HR4 Column, 5 µm, 4.6 × 300 mm, Styragel HR2 Column, 5 µm, 4.6 × 300 mm, and Styragel HR0.5 Column, 5 µm, 4.6 × 300 mm) and calibrated with polymethylmethacrylate standards. Signals were detected with a RI detector. Thermogravimetric analysis (TGA) was conducted with a Perkin Elmer TGA7 at a heating rate of 20 °C min⁻¹ under nitrogen gas flow up to 800 °C. Scanning electron microscopy was conducted on a FEI NovaNanoSEM 230 at 10–15 kV acceleration voltage after the samples were sputtered with 7 nm of platinum. SEM particle size was determined by measuring the diameter of 50 neighboring particles in a representative area. Dynamic light scattering (DLS) was done with a Malvern Zetasized Nano ZS, where the results were averaged from 3 separate measurements. Differential scanning calorimetry (DSC) measurements were done on a Perkin Elmer DSC 8000. The DSC cycle consisted of two heating steps from 20 °C to 200 °C and a cooling step from 200 °C to 20 °C at a rate of 20 °C min⁻¹. For the broadband dielectric spectroscopy (BDS) measurements a Novocontrol high impedance Alpha Analyzer was coupled to a Anton Paar MCR rheometer. The rheometer plates (Ø=25 mm), which were electrically isolated from the rest of the device, served as electrodes. The sample height was equivalent to the gap width which was controlled by the rheometer software. This setup allowed measurements of samples in the melt state.

2.3 Inverse miniemulsion polymerization of PHEMA/Dipole

A solution of poly(ethylene-*co*-butylene)-block-poly(ethylene oxide) surfactant and α,α' -azobisisobutyronitrile (AIBN) in cyclohexane (CH) continuous phase and a solution of DR1 or DR1MA in hydroxyethyl methacrylate (HEMA) dispersed phase were prepared. To dissolve quantities of DR1 or DR1MA above the solubility limit of HEMA, NMP co-solvent was used. For the quantities used, see Table 1. The two solutions were mixed together and stirred at room temperature to

obtain a homogenous macroemulsion. The miniemulsion was produced by subjecting the macroemulsion to high shear forces using a Sonics Vibra-cell™ VCX 750 ultrasonicator at 40% power output (300 watt) for 5 min while being immersed in an iced water bath. The miniemulsion was bubbled through with Ar, and then stirred under inert atmosphere in a preheated bath at 72 °C. After 24 h, the resulting suspension was cooled to room temperature.

Table 1. Preparation of PHEMA using miniemulsion polymerization.

Sample	HEMA	Dye		Dye/HEMA		NMP	CH	Surfactant	AIBN
	[g]	Type	[mg]	[wt%]	[g]	[g]	[mg]	[mg]	[mg]
A	1.5	—	—	0	—	6	50	100	
B1	1.5	DR1	20	1.3	—	6	50	100	
B2	0.5	DR1	66	11.8	0.5	8	36	66	
B3	0.5	DR1	100	16.6	0.5	8	36	66	
C1	1.5	DR1MA	20	1.3	—	6	50	100	
C2	0.75	DR1MA	50	6.3	—	6	25	50	
C3	0.75	DR1MA	100	11.8	—	6	25	50	
C4	0.5	DR1MA	133	21.0	0.25	6	50	25	
C5	0.5	DR1MA	150	30	0.5	8	50	33	

The particles were characterized *via* SEM, DLS, DSC, TGA and ¹H NMR in DMF-d₇. DLS measurements were performed on the dispersions which were diluted several times while SEM samples were done by taking a drop of the dispersion and letting it dry on a sample holder. The other measurements were done from filtered samples. Some selected samples were dried at high vacuum and pressed to 25 mg pellets in order to measure their impedance with the rheometer setup. The pellets were heated to 195 °C, well above the *T_g* of the samples, upon which the isolated rheometer plate was lowered to contact the sample in melt state at a determined sample height. Impedance spectra were obtained at 10 °C intervals from 195°C to 25°C. The measurement was deemed acceptable when the sample was found in a monolithic, bubble-free state after the removal of the rheometer plate.

2.4 Composites of PHEMA/Dipole particles in PDMS

PDMS composites with 50 wt% of selected particles were produced by adding the PDMS matrix and (25-35% methyl hydrosiloxane)-dimethylsiloxane-copolymer crosslinker (XL) to a dispersion of particles in CH under stirring (see Table 2). When a homogeneous dispersion was formed, dibutyltin dilaurate (DBTL) catalyst was added and films were then produced with the doctor blade method using a Zehntner ZUA 2000 set at 300 µm gap height. After drying the films at 80°C for several days, thin films with thicknesses around 100 µm were obtained. The dispersion quality of the composites was verified by freeze-breaking them in liquid nitrogen and examining the platinum sputtered fracture surface *via* SEM.

Table 2. Preparation of HEMA/PDMS composite films.

Sample	Particle		PDMS		XL	DBTL	CH
	Type	[g]	[wt%]	[g]	[µl]	[µl]	[g]
C-A	A	0.5	50	0.5	50	10	3
C-C3	C3	0.5	50	0.5	50	10	3

3. RESULTS AND DISCUSSION

3.1 PHEMA/Dipole particles: composition and particle size determination

The maximum dipole concentration in the particles is generally limited by their solubility in the dispersed phase. As such, DR1 could only be incorporated at 1.3 wt%. While it has been possible to significantly increase the DR1 content in the miniemulsion from 1.3 wt% to 11.8 wt% when using NMP co-solvent, a further increase in the dipole content lead to

large flakes in the miniemulsion after polymerization. By using a methacrylate-functionalized DR1 the solubility of the dipole could also be increased to 11.8 wt%. As can be seen in the SEM images (Figure 2) the polymerization produced particles in the sub-micrometer range. Their sizes according to the SEM images and DLS number size distribution are noted in Table 3. Again the DR1MA content can be raised to 21 wt% with NMP co-solvent, above which the emulsion becomes unstable over the time-period of the polymerization. While the dipole content could possibly be further optimized by changing the nature and the amount of co-solvent, this was not further attempted.

Figure 2. SEM images of PHEMA particles containing dipoles.

It was found that spherical particles were obtained when encapsulating DR1 without NMP. In contrast, the particles produced with a co-solvent, while still roughly spherical, have a less uniform shape and are flattened against the substrate in the SEM image. This makes them seem larger (820 nm) than compared to the particles produced without co-solvent (480 nm), but DLS shows that they are of roughly the same size when in solution. A systematic investigation of the influence of the dipole on the particle size was not carried out, but it seems from the data in Table 2 as if the dipole has no noteworthy effect on such.

The NMR spectra (Figure 3) were recorded using particles obtained by filtering the dispersion and subsequently washing the particles with CH. The spectra confirm the formation of PHEMA and PHEMA-DR1MA copolymer, as well as the presence of DR1. The amount of dipole incorporated into the particles corresponds to the amount in the miniemulsion prior to the polymerization. The molecular weight and the PDI of the prepared polymers can be found in Table 3. The PHEMA sample A has a molecular weight of 95'000 g/mol and a polydispersity index (PDI) of 2.1. The addition of dipoles generally causes the PDI to increase, up to a PDI of 8.4 for sample C4. Data on the thermal transitions and stability of the samples A and C1 to C4 can be found in Table 4 as determined by DSC and TGA. The low thermal stability of C4 can be attributed to the presence of NMP.

Due to the limited amount of DR1 which can be encapsulated in PHEMA, even with a co-solvent, it was deemed best to focus future efforts on the copolymer system.

The particles form stable dispersions in CH directly after the polymerization. By using these dispersions directly to produce composites in PDMS, agglomeration of the particles was avoided. This is evident by the homogeneous particle distribution within the composites C-A and C-C3 (Figure 4).

Table 3. Size and GPC results for the PHEMA samples.

Sample	Particle diameter		M_n [kg mol ⁻¹]	PDI
	SEM [nm]	DLS [nm]		
A	570± 80	650± 80	95	2.1
B1	480 ± 40	510 ± 200	193	4.2
B2	820 ± 110	540 ± 170	92	2.1
B3	N/A	N/A	—	—
C1	480 ± 50	560 ± 180	186	4.0
C2	550 ± 100	520 ± 90	105	5.7
C3	570 ± 70	660 ± 130	96	5.5
C4	750 ± 90	560 ± 100	69	8.4
C5	N/A	N/A	—	—

Table 4. Glass transition temperature (T_g) and decomposition temperature (T_d) as determined by DSC and TGA.

Sample	T_g [°C]	T_d [°C]
A	96	415
C1	93	380
C2	96	350
C3	92	335
C4	65	290

Figure 3. ¹H NMR spectra of the PHEMA particles without (A) and with DR1 dipoles (B1, B2) and of the PHEMA-co-DR1MA particles (C1-C4) produced by miniemulsion polymerization.

Figure 4. SEM images of the composites C-A and C-C3

3.2 PHEMA/Dipole particles: BDS-analysis

Figure 5. Imaginary permittivity (ϵ'') versus temperature for samples A and C3 as measured by BDS.

Impedance measurements (Figure 5) were done on PHEMA samples (A) and on PHEMA-*co*-DR1MA samples with the maximum dipole content produced without co-solvent (C3). Data for sample A reveals a relaxation behavior identical to the reported behavior of bulk PHEMA.^{19,20} The surfactant therefore has no influence on the relaxation behavior of the polymer. The spectrum is dominated by a rapidly increasing ϵ'' signal at low frequencies (0.5-10⁴ Hz) which is mirrored by a rapid increase in ϵ' . This behavior is typically attributed to electrode polarization due to conductivity contributions of the sample. A single peak is visible at high frequencies (10⁵ – 10⁶ Hz) which was speculated to be either a β -relaxation peak or the $\alpha\beta$ -merge peak.¹⁹ A shoulder to the electrode polarization contribution is visible at lower frequencies (1 - 100 Hz) which was attributed to the β relaxation.²⁰ These assertions can be partially substantiated by analyzing the data with

the phenomenological Havriliak-Negami (HN) function,²¹ $\epsilon^* = \epsilon_\infty + i \frac{\sigma_{dc}}{\epsilon_0 \omega} + \sum \frac{\Delta \epsilon_n}{\{1 + [i\omega\tau_n]^{1-\alpha_n}\}^{\beta_n}}$, where ϵ^* is

the complex impedance, ϵ_∞ the high frequency permittivity, σ_{dc} the dc-conductivity, ϵ_0 the vacuum permittivity. $\Delta \epsilon_n$ and τ_n are the relaxation strength and mean relaxation time, the parameters α_n and β_n describe the width and asymmetry of the dielectric loss peak ϵ'' of process n. The conductivity contribution to ϵ^* is relatively important here as the β - and the $\alpha\beta$ -merge peak both merge with the dc contributed part. Unfortunately the spectra for C3 at temperatures where the $\alpha\beta$ -merge peak is relevant were not resolved enough to apply the HN-fit.

Figure 6. Real conductivity part of samples A and C3 at different frequencies as measured by BDS.

As a matter of practicality, σ_{dc} was taken as the conductivity at 0.5 Hz, the lowest measured frequency. At temperatures below 100 °C that value was slightly different from σ_{dc} , as the conductivity was showing the beginnings, but has not reached a steady state yet (Figure 6). It follows that in order to fit data taken at temperatures below 100 °C the high frequency part of the spectra was given more weight, as can be seen representatively in Figure 7. Above 100 °C, σ_{dc} could accurately be measured by the conductivity value at 0.5 Hz as it has reached a steady state.

Figure 7. Cole-cole plot of four representative relaxation curves of sample A (left) from which the dc-contribution has been subtracted (scatter plot) and their fit-curves according to the HN-function (line-plot) and the temperature dependent mean relaxation time τ_n extracted from the fitted HN-functions for samples A and C3 (right).

The β relaxation hinted at in the imaginary permittivity plot can be quantified after extracting the fit-parameters. The evolution of τ with temperature (figure 7) suggests an Arrhenius-type relaxation process typically associated with sidechain movements. The activation energy for this process has been calculated to be 48.4 ± 5.8 kJ/mol in sample A and 47.4 ± 3.7 kJ/mol in sample C3, which indicates that the $\beta(A)$ and $\beta(C3)$ can be assigned to the same side-chain relaxation process. Unfortunately the relaxation peak corresponding to the relaxation of the dipole was not resolved in the measured range of the current experiment.

CONCLUSIONS

DR1 dipole was successfully incorporated into PHEMA particles using miniemulsion polymerization. The maximum dipole concentration is limited by the solubility of the dipole in the dispersed phase. The concentration of the dipole can be increased by either chemically modifying the dipole or using a co-solvent in the dispersed phase. The incorporation of the dipole was confirmed with ^1H NMR and matched mostly with the target concentration. Particle size distributions were reasonably narrow, while the inclusion of the dipole and the use of a co-solvent don't seem to influence the particle size. BDS analysis reveals that particles produced in such a manner do not exhibit any additional relaxation phenomena. The β relaxation of the hydroxyethyl-side chain was revealed and quantified in both the pure PHEMA sample and the sample containing dipoles. The $\alpha\beta$ -merge peak was observed in both samples but could only be quantified for the pure PHEMA sample. Unfortunately the relaxation of the dipole was not resolved in the measurement range, due to the typically large conductivity-contribution in PHEMA. It has been shown that the relaxation phenomena in PHEMA do not change significantly when being produced by miniemulsion polymerization and when dipoles are incorporated.

The polymerized particles form stable dispersions in cyclohexane which allow formation of homogeneous PHEMA-PDMS composites. Further investigations into the relaxation behavior of the particles and the composite are needed; especially the dipole relaxation has to be identified, if the system is to be developed further.

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