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A new way of improving non-linear optical properties of side-chain non-linear optically active copolymers

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A new set of side-chain non-linear optical copolymers containing two different amounts of 2-methyl-4-nitroaniline (MNA) and disperse red 1 (DR1) chromophores are reported. From this set of copolymers, it is easy to see how to optimize such key properties as glass transition temperature, maximum absorption wavelength and second harmonic signal, d_{33}. The composition dependence of these properties is seen to vary linearly with MNA and DR1 content.

(Keywords: non-linear optics; side-chain copolymers; optimization)

INTRODUCTION

The development of non-linear optical polymeric materials has been intensive because they offer such advantages as being much easier to process and having higher mechanical and environmental stability than either inorganic or organic non-linear optical crystals[1–3]. Those non-linear optical polymers can be synthesized in different structures, such as guest–host[4], side-chain or main chain[5–7], and crosslinked structures[8,9]. The guest–host and crosslinked systems have been known to suffer from a limitation of the amount of chromophores that can be incorporated into the polymer matrix[10–12]. In contrast, the attainable functionalization is much higher in the case of either side-chain or main chain systems. However, it is much more difficult to synthesize main chain than side-chain systems.

An interesting example of a side-chain non-linear optical polymer utilizes disperse red 1 (DR1) as the non-linear optical chromphore. Such a polymer, reported by Hill *et al.*[13], is polyacrylic acid derivatized with DR1. It has a high linear electro-optic coefficient (r_{33}) of about $30\,\mathrm{pm\,V^{-1}}$, but its glass transition temperature, T_g, is only about 82°C, which leads to loss over time of non-linear optical activity even at room temperature. Sperling *et al.*[14] have made an analogous side-chain non-linear optical polymer utilizing 2-methyl-4-nitroaniline (MNA) as the non-linear optical chromophore. Although this polymer has a high T_g of about 205°C (and therefore excellent stability at room temperature), its second harmonic signal is unfortunately quite low ($d_{33} \sim 3\,\mathrm{pm\,V^{-1}}$) even though its functionalization level is already high (~ 85%). We have investigated how we might optimize T_g and d_{33} in a single copolymer by incorporating both of these non-linear optical chromophores into a single macromolecule. The idea is similar to the blending of two polymers, namely to achieve a combination of useful properties from the two polymers. However, no phase separation should be expected in our system since the two chromophores are attached to the backbone of a copolymer[6].

EXPERIMENTAL

Synthesis

Poly{*N*-MNA acrylamide-*co*-4′-[[2-(acryloyloxy)ethyl]-ethylamino]-4-nitroazobenzene} or PM*x*D*y* ($10x$ = mol% MNA and $10y$ = mol% DR1) was synthesized from poly(acryloyl chloride) MNA and DR1 using 1,4-dioxane as the solvent. Through nucleophilic addition-elimination reaction as shown in *Figure 1*, the chloride group in poly(acryloyl chloride) is replaced by MNA and DR1. The amount of attached chromophores to the polymer backbone determines the functionalization level of our non-linear optically active copolymers.

A mixture of 2.5 g poly(acryloyl chloride), 3.24 g MNA, and 1.68 g DR1 was dissolved in 1,4-dioxane to produce PM8D2 (i.e. the acrylate copolymer whose side groups are 80% MNA and 20% DR1). It was stirred under a nitrogen atmosphere at room temperature overnight to make sure that the reaction was completed. The environment where the mixing and reaction took place was controlled carefully to ensure there was no water contamination from the surroundings. Water can react with poly(acryloyl chloride) to form poly(acrylic acid). The mixture was poured into a dilute solution of $NaHCO_3$ to neutralize hydrochloric acid resulting from the reaction. The product was filtered through filter paper, washed with methanol to remove unreacted chromophores, and vacuum dried at 105°C overnight. The resulting copolymer was further purified by recrystallization involving pyridine and methanol. The red

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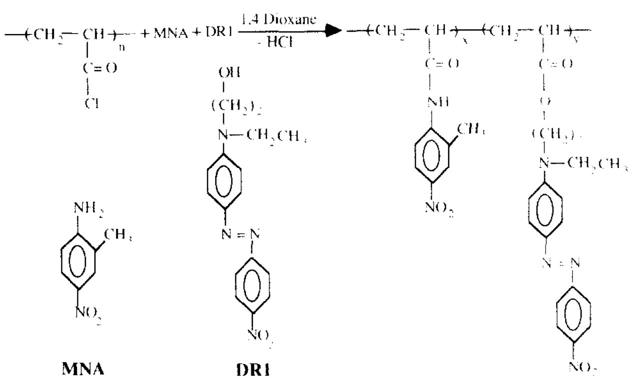

Figure 1 Synthesis of poly{N-MNA acrylamide-*co*-4′-[[2-(acryloyloxy)ethyl]ethylamino]-4-nitroazobenzene}

solid product was again filtered, washed with methanol, and vacuum dried at 105°C for a day. The purification was repeated to make sure that no unreacted chromophores or other impurities were present in the copolymer.

The product was verified using elemental analysis by Oneida Research Services, Inc. Its structure was further verified using Fourier Transform Infrared (*FT*-i.r.) analysis. All the spectra were recorded at room temperature in the region 500–3700 cm^{-1}.

Thermal analysis was conducted on a Perkin-Elmer Differential Scanning Calorimeter (DSC-7) equipped with a computerized data station. A heating rate of 10°C min^{-1} was used, and the glass transition temperatures recorded as the mid-point of the change in heat capacity. The average weight of the samples used in the measurement was about 10 mg. Prior to the d.s.c. measurement, the samples were vacuum dried at a temperature a little above their predicted T_g to make sure there was no residual solvent.

The degree of polymerization of the copolymers was found by the intrinsic viscosity method to be about 100. This number indicates that the molecular weight of the copolymers is rather low.

The u.v.-visible absorbance of both unpoled and poled PMxDy samples was measured over the wavelength range 260–900 nm. It was necessary to subtract the strong background from indium tin oxide (ITO)-coated glass. The thickness of the copolymer samples was approximately 1 μm.

Thin film fabrication and poling

To make thin films of the copolymers, a solution of PMxDy in pyridine with average concentration of about 12% was spin coated onto ITO-coated glass (1.5 × 1.5 cm^2). The thickness of the ITO layer was about 25 nm (manufacturer's data). The solution was filtered by using a disposable syringe filter with a pore size of 5 μm in order to remove any undissolved impurities which may have been present. The ITO-coated glass was cleaned using chromic acid, rinsed with distilled water, and vacuum dried at 100°C for a few hours. Film thicknesses were measured using an Alpha-Tencore 200 step profiler and were in the range 0.5–1 μm. The polymer films are smooth and transparent.

Samples were then mounted in an apparatus that allowed us to pole (and therefore to develop a non-centrosymmetric orientation of chromophores) and to measure the second harmonic generation of light passing through them. Films were poled by a corona developed by a tungsten needle placed about 1 cm from the surface of the sample. The applied voltage in this experiment is 4.0 kV; the current flowing through the tungsten needle never exceeded 1 mA. After the film was poled at a temperature slightly above T_g for about 15 min, it was cooled to room temperature with the field on in order to freeze the chromophore alignment. The generated second harmonic beam at 532 nm, during poling and for the time elapsing after the poling field was turned off, was then measured for its intensity. The laser source used for second harmonic measurements had a wavelength of 1064 nm and pulse width of about 5 ns with a repetition rate of 10 Hz.

Non-linear optical parameters

The second-order non-linear d coefficients (d_{33}) for these copolymers were evaluated from the average of second harmonic relative signals measured during corona poling. The second harmonic signals of poled samples were further measured as a function of incident angle of the laser beam using the Maker fringe technique[15,16].

The intensity of the second harmonic signal generated by a fundamental beam with intensity I_ω is given by[17,18]:

$$I_{2\omega} \propto \left[\frac{l^2 I_\omega^2 d_{\mathrm{eff}}^2}{n_\omega^2 n_{2\omega}}\right] \sin^2\left[\frac{\pi L/2L_c}{(\pi L/2L_c)^2}\right] \tag{1}$$

where L is the film thickness, d_{eff} is the effective second-order non-linear d coefficient, n_ω and $n_{2\omega}$ are the refractive indices at frequencies ω and 2ω, respectively, and L_c is the coherence length of the non-linear media. For thin films ($L \ll L_c$), the factor $\sin^2[(\pi L/2L_c)/\pi L/2L_c)^2]$ becomes 1. Thus, equation (1) is reduced to:

$$I_{2\omega} \propto \left[\frac{l^2 I_\omega^2 d_{\mathrm{eff}}^2}{n_\omega^2 n_{2\omega}}\right] \tag{2}$$

In the poling experiment, the ratio of second harmonic relative signals in the samples (I_s/I_o) to that of a reference (α-quartz) (I_Q/I_o) was measured. By simple modification of equation (2), d_{eff} can be derived, as given by the following equation:

$$d_{\mathrm{eff}} \propto d_{11}\left[\frac{I_s/I_o}{I_Q/I_o}\right]^{1/2}\frac{L_Q}{L_s}\left[\frac{n_s^2(2\omega)n_s(\omega)}{n_Q^2(2\omega)n_Q(\omega)}\right] \tag{3}$$

where L_Q and L_s are the coherence length of quartz (20.6 μm)[16] and film thickness, respectively and d_{11} is the second order d coefficient of quartz (0.34 pm V^{-1})[19]. The subscripts s and Q represent film and quartz, respectively. The effective non-linear d coefficient is also given[20] by:

$$d_{\mathrm{eff}} = d_{33}\sin^2\phi_\omega \sin\phi_{2\omega} + d_{31}\cos^2\phi_\omega \sin\phi_{2\omega} + 2d_{15}\sin\phi_\omega \cos\phi_\omega \cos\phi_{2\omega} \tag{4}$$

where ϕ_ω and $\phi_{2\omega}$ are the angles of refraction of the fundamental and second harmonic beams, respectively. They can be related to the incident angle ϕ by using an equation derived from Snell's law: $\sin\phi_\omega/\sin\phi_{2\omega} = n_{2\omega}/n_\omega$. Using the Kleinman symmetry assumption[2,16], $d_{31} = d_{15}$ and $d_{31} = 1/3d_{33}$, d_{33} can be found from the measured values of d_{eff}.

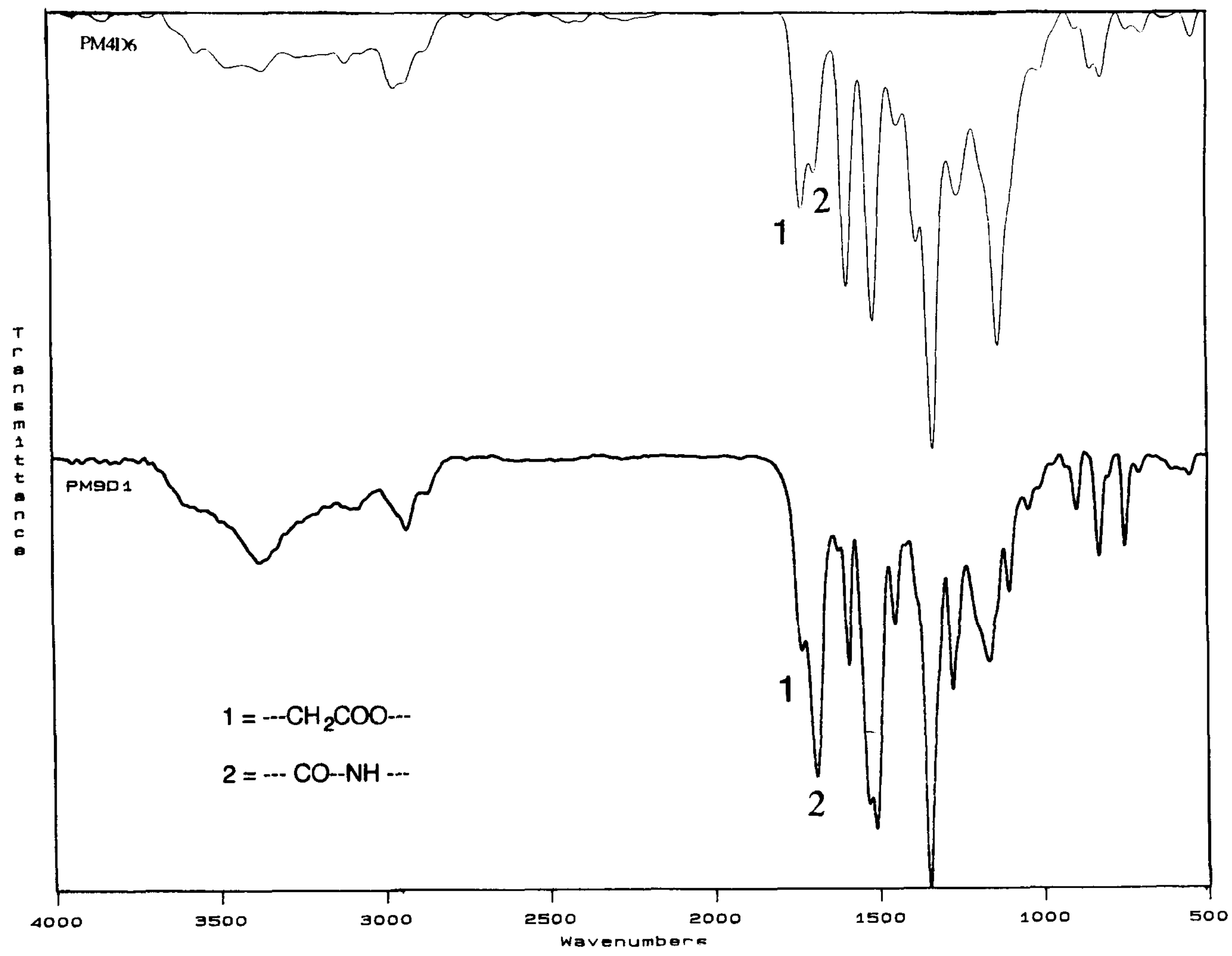

Figure 2 I.r. spectra of PM9D1 and PM4D6

Table 1 Elemental analysis data for PMxDy copolymers

	Theoretical (%)			Found (%)		
Copolymers	C	H	N	C	H	N
PM9D1	58.57	4.95	13.76	57.82	4.92	11.3
PM8D2	58.94	5	13.92	57.89	5.24	11.43
PM6D4	59.68	5.1	14.24	59.13	5.17	12.43
PM4D6	60.42	5.2	14.56	59.35	5.2	12.23
PM1D9	61.53	5.35	15.04	60.29	5.33	13.16

In the case of copolymers which have high absorption in the region of the second harmonic wavelength, it is necessary to multiply d_{33} by an absorption correction factor[21]:

$$A(2\omega) = \frac{\alpha t}{[1 - \exp(-\alpha t)]\exp(-\alpha t/2)} \qquad (5)$$

where α is the absorption correction, t is film thickness, and $A(2\omega)$ is the absorption correction factor at the second harmonic wavelength.

RESULTS AND DISCUSSION

Characterization to establish the structure of our copolymers has been done using elemental analysis and *FT*i.r. analysis. Elemental analysis (*Table 1*) verifies the functional level of the copolymers. Major peaks in the *FT*i.r. spectra, such as –CONH– (~ 1690 cm^{-1}), –CH$_2$COO– (~ 1730cm^{-1}), and –N=N– (~ 1600cm^{-1}), are consistent with the intended structures of those copolymers. No peak belonging to –COCl–, at wavenumbers 1770–1815 cm^{-1}, can be found; this indicates that we have accomplished complete substitution of –Cl in poly(acryloyl chloride). The i.r. spectra of PMxDy, such as PM1D9, PM4D6, PM6D4, PM2D8 and PM9D1, are all similar, only varying systematically according to composition. As an example, the i.r. spectra of PM9D1 and PM4D6 are shown in *Figure 2*. The i.r. spectrum of PM9D1 shows that its –CONH– peak at 1690 cm^{-1} is greater than the –CH$_2$COO– peak at 1730 cm^{-1}, because it has higher MNA content. On the other hand, due to the higher DR1 content in PM4D6, its –CONH– peak is less than its –CH$_2$COO– peak.

The results of d.s.c. thermal analysis indicate that all the polymers of this study are homogeneous glasses, characterized by a single T_g. Their T_g is found to be higher than that of PM0D10 (82°C)[13] and lower than that of PM8D0 (205°C)[14]. The plot of T_g *versus* mol% MNA (x) in PMxDy is shown in *Figure 3*. The linear relationship between T_g and mol% of MNA seems to obey the classical Flory–Fox relationship. No evidence for the presence of crystallinity, namely melting point,

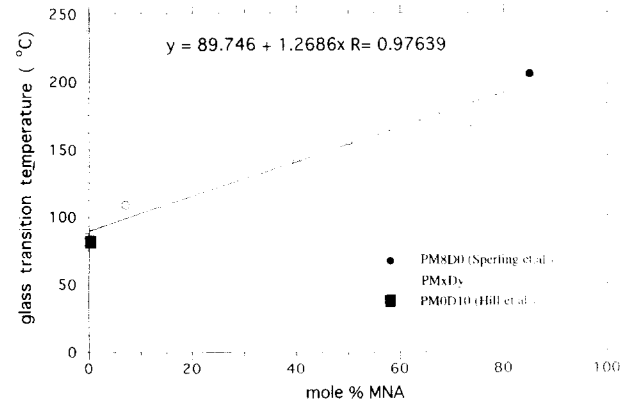

Figure 3 Plot of T_g vs. mol% MNA of PMxDy copolymers

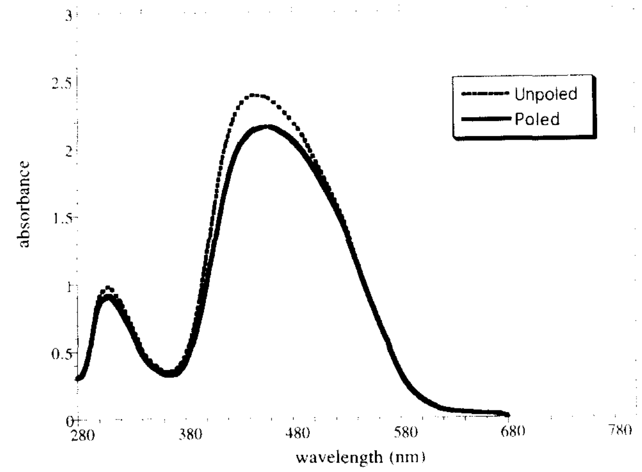

Figure 4 U.v.-visible spectra of unpoled and poled PM1D9

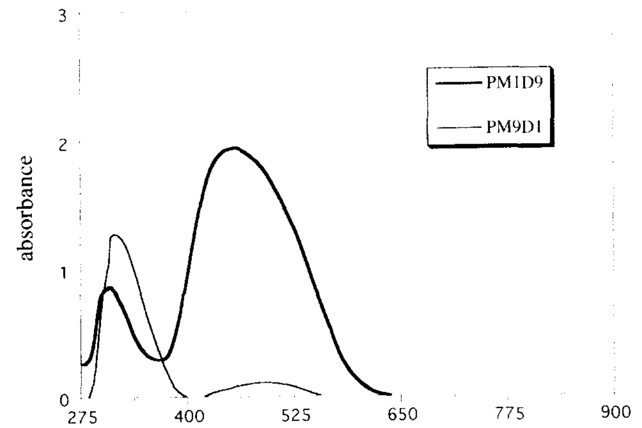

Figure 5 The absorbance of poled PM1D9 and PM9D1 as a function of wavelength measured at room temperature

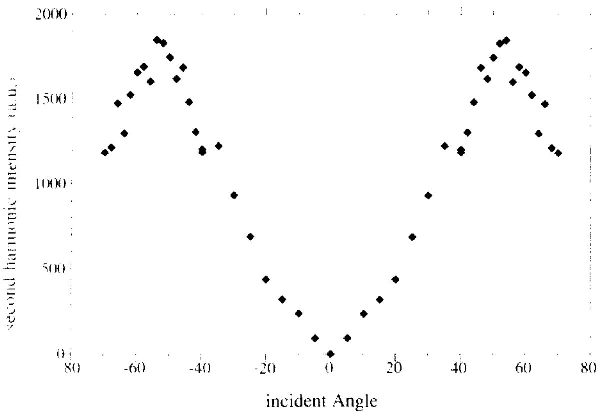

Figure 6 The second harmonic signal as a function of angle of incidence of laser beam (1064 nm) measured at room temperature

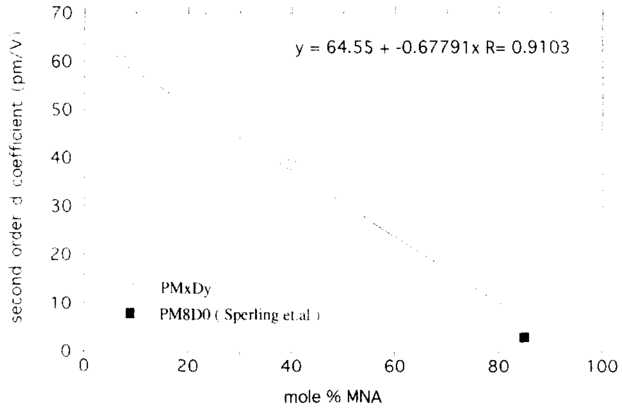

Figure 7 Plot of d_{33} vs. mol% MNA of PMxDy copolymers

was found in any of the d.s.c. scans. The samples were further verified to be completely amorphous using polarized microscopy.

Figure 4 shows the measurement of u.v.-visible absorption spectra of unpoled and poled PM1D9, which indicate that its absorptivity diminishes due to poling. Electric poling has been reported (see, for example, ref. 20) to be able to change the absorbance of a system. The changes are likely to be a measure of the degree of orientation of the chromophores in that system. The absorbance of other copolymers with different x exhibits analogous behaviour.

There are two maximum absorption wavelengths (λ_{max}) of PMxDy samples, one is about 310 nm and another 470 nm. The u.v.-visible absorption spectra of poled PM9D1 and PM1D9 are illustrated in *Figure 5*. The λ_{max} of 310 nm and 470 nm indicate the presence of MNA and DR1 chromophores, respectively. As reported by Amano *et al.*[22], the λ_{max} of DR1-substituted copolymers was reported to be about 470 nm. Moreover, the λ_{max} of highly functionalized MNA-substituted copolymers was reported to be about 310 nm by Sperling *et al.*[14] The spectrum of PM9D1 shows that the absorbance at 310 nm is higher than that at 470 nm, indicating that PM9D1 has more MNA than DR1. On the other hand, the spectrum of PM1D9 shows that the absorbance at 470 nm is higher than that at 310 nm due to higher DR1 content in this copolymer.

In Maker fringe experiments, the specimen was rotated about a principal axis perpendicular to the laser beam. *Figure 6* illustrates the angular dependence of the second harmonic signal of PM6D4. We could not see any fringes because the thickness of our samples is much smaller than the coherence length of the non-linear media.

It has been reported that high d_{33} can be readily achieved even at low chromophore content (10–20%) for DR1-functionalized copolymers. The d_{33} of 10% DR1-substituted poly(methyl methacrylate) (DR1/PMMA) is

Table 2 Recalculated mole percentage of DR1 and MNA in PMxDy copolymers

	Expected (%)		Actual (%)		
Copolymers	MNA	DR1	MNA	DR1	AA
PM9D1	90	10	80	2.5	17.5
PM8D2	80	20	73	10	17
PM6D4	60	40	50	37	13
PM4D6	40	60	40	45	15
PM1D9	10	90	7	80	13

found[23] to be about 43 pm V^{-1} with corona poling (unspecified applied field). Moreover, Esselin *et al.*[24] reported the d_{33} of their DR1/PMMA copolymers to be about 32 pm V^{-1} (10% DR1) and 57.9 pm V^{-1} (19% DR1). It has been reported by Hill *et al.*[13] and Xie *et al.*[25] that 100% DR1-functionalized homopolymer (PM0D10) can have a high electro-optic coefficient (r_{33}) of about 30 pm V^{-1} using a poling field of 20 MV m^{-1} and 633 nm He–Ne laser source.

The results of our non-linear d coefficient measurements are illustrated in *Figure 7*. The figure shows that the d_{33} values of these 10% and 20% DR1-substituted copolymers (PM9D1 and PM8D2) are lower than the reported results. We suspect that there may be some unsubstituted sites on these chains. These unreacted acryloyl chloride groups will convert into acrylic acids during the purification work-up. The results of elemental analysis shown in *Table 1* indicate that the amount of nitrogen and carbon found is lower than the theoretical value calculated under the assumption that all of the chromophores supplied are reacted with all of the acryloyl chloride groups available. Then, from the results of elemental analysis, we recalculated the mole percentage of DR1, MNA and acrylic acid (AA) in the copolymer. It is shown in *Table 2* that PM9D1 and PM8D2 have lower DR1 content than expected under our previous assumption of full substitution. Therefore it is reasonable to say that the discrepancy in d_{33} values mentioned earlier is mostly due to the unexpected presence of a few acrylic acid sites. Furthermore, of our PMxDy copolymers, we found that PM8D2 has the optimal values of T_g and d_{33}, at approximately 165°C and 34 pm V^{-1}. However, we believe that those properties can be further increased by increasing the percentage of DR1 (up to 20%) while keeping the percentage of MNA as high as possible (up to 80%).

The d_{33} of the new copolymers with 10% and 20% DR1 is supposed to be higher than that of 10% and 20% DR1-substituted methyl methacrylate copolymers since these new copolymers are functionalized with two chromophores. For example, PM8D2, besides its 20% DR1 content, also has 80% MNA (assuming all chromophores are completely reacted). The copolymer with 85% MNA attached to its polymer backbone can have d_{33} of about 3 pm V^{-1} as reported by Sperling *et al.*[14]. Thus PM8D2 should have d_{33} that is a little higher than a copolymer which is functionalized only with 20% DR1. However, this has not been seen yet, possibly for the reason mentioned earlier.

In this study, we have shown that the stability of chromophore alignment in copolymers functionalized only with DR1 can be enhanced by introducing another chromophore (MNA). In addition, the second-order non-linear d coefficient of copolymers functionalized only with MNA can be improved by incorporating DR1 into them. So, by synthesizing new copolymers whose side groups are an appropriate combination of DR1 and MNA, it is possible to optimize both their T_g and d_{33} values. The high d_{33} in our new copolymer systems is mainly due to DR1 non-linear chromophores because the hyperpolarizability (β) of DR1 is eight times higher than that of MNA[26,27]. However, the high T_g in our copolymer systems is mainly due to the strong intermolecular forces developed between the MNA moieties.

Furthermore, incorporating two different chromophores in a single macromolecule gives one the ability to influence linear optical properties, such as absorbance bands, λ_{max}. The absorbance at the second harmonic wavelength (532 nm) can be kept as low as possible by having a small amount of DR1 in the system while keeping considerably high values of d_{33} and T_g. Because different dyes have different λ_{max}, having multiple dyes in a polymer can allow us to create a device which is capable of filtering multiple wavelengths of light. For example, our copolymers can be used to filter light with wavelengths of about 300 nm and 500 nm. Therefore, this set of multiple-chromophore copolymers, besides demonstrating how to optimize properties for non-linear optical devices, shows us how to tailor linear optical properties, such as might be needed in a multiple wavelength filtering device.

CONCLUSIONS

The design of side-chain copolymer systems for second-order non-linear optical applications depends on functionalization level, dipole moment and polarizability of incorporated chromophores, poling field, T_g, absorption maximum wavelength and poling efficiency. Improving those parameters will result in useful non-linear optical polymers for future optical devices. The combination of two different chromophores in certain compositions can be used to optimize the non-linear optical properties such as T_g and d_{33} of a copolymer which is functionalized with only one of the chromophores. Thus, instead of having either a copolymer with low T_g and high d_{33} or a copolymer with high T_g and low d_{33}, copolymers with high T_g and high d_{33} can be produced.

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