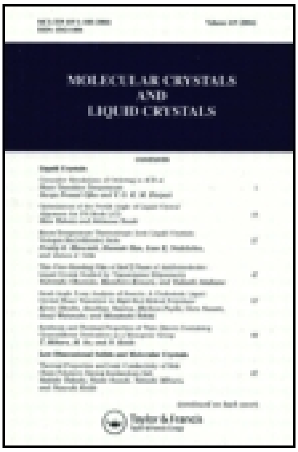

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Development of Thermally Stable Novel EO-polymers

Takami Ushiwata [a], Etsuya Okamoto [a] & Toshikuni Kaino [a]

[a] Institute of Material Research for Advanced Materials, Tohoku University, Sendai, 980-8577, Japan

To cite this article: Takami Ushiwata, Etsuya Okamoto & Toshikuni Kaino (2002): Development of Thermally Stable Novel EO-polymers, Molecular Crystals and Liquid Crystals, 374:1, 303-314

To link to this article: http://dx.doi.org/10.1080/10587250210421

Mol. Cryst. Liq. Cryst., Vol. 374, pp. 303-314
Copyright © 2002 Taylor & Francis
1058-725X/02 $12.00 + .00

Development of Thermally Stable Novel EO-polymers

TAKAMI USHIWATA, ETSUYA OKAMOTO and
TOSHIKUNI KAINO

*Institute of Material Research for Advanced Materials,
Tohoku University, Sendai, 980-8577, Japan*

We have synthesized and evaluated NLO properties of azo dye attached novel NLO polymers with high thermal stability. The NLO polymers containing an azo dye, DR-1, in their side-chain were synthesized using a new approach. Polyacrylic acid or polymethacrylic acid reacted with DR-1 via the intermediate reaction of the acid and N,N'-dicyclohexylcarbodiimide. The DR-1 contents of the products were 39mol% and 29mol%, for derivatives from polyacrylic acid and polymethacrylic acid, respectively. Glass transition temperatures of 150°C to 170°C were obtained for Disperse red 1 dye attached polymethacrylic acid. The poled film exhibited second order NLO susceptibilities ($\chi^{(2)}{}_{33}$) of 48pm/V to 53pm/V at 1.3μm fundamental wave. Due to the high glass transition temperatures of the polymers, long-term stability of the optical nonlinearity at 100°C was observed for 200 hrs or more. However residual carboxyl groups caused absorbance decrease mainly by hydrolysis of the ester bonds of the polymers. These polymers can be further improved to have more thermally stable structure by heat treatment. Through the approach, methacryl imide structure was formed and the polymer has high Tg of 165?. This imidized polymer exhibited $\chi^{(2)}{}_{33}$ of 45 pm/V at a wavelength of 1.3μm and maintained about 90% of the initial value after 230 hrs or more at 100°C.

Keywords: second order nonlinear optics, nonlinear optical polymers, thermal stability, polymethacrylic acid, polyacrylic acid, azo dye, Disperse red 1, imidization

INTRODUCTION

Polymeric materials with highly polarizable electronic systems can exhibit larger nonlinear optical (NLO) response than that for inorganic materials e.g. $LiNbO_3$. So, they are of considerable interest for the development of electro-optic and all-optic photonic devices due to such other potential advantages as ultrafast response and ease of processing[1]. However, to be useful in optical device applications, the second order NLO response must be stable at elevated temperatures and optical loss at operational wavelengths should be minimized.

Insufficient long-term stability of NLO susceptibility due to relaxation of induced polar order of NLO chromophores at elevated temperatures is a major problem in polymeric NLO devices development. Mainly two different approaches have been proposed to suppress this relaxation of the chromophores. One is to synthesize side-chain NLO polymers with high glass transition temperatures (T_gs) using polymers with rigid main-chain structures[2,3]. The other is to introduce crosslinked systems into NLO materials[4-6]. Polymethylmethacrylate (PMMA) is a typical polymer matrix for NLO polymer investigation and optical device fabrications. However, PMMA with NLO active chromophores synthesized so far don't possess T_gs high enough for actual applications except for a few examples[7].

In this work, NLO chromophore attached polymethacrylates with high T_gs were synthesized using polymethacrylic acid (PMAA) or polyacrylic acid (PAA) as starting materials. Their optical properties and long-term stabilities of the induced polar order at elevated temperature were investigated. PMAA and PAA possess high T_gs relative to PMMA based NLO materials, though, to our knowledge, limited features of these polymers as NLO polymer matrix has been reported[8,9]. To synthesize these NLO polymers, a new approach of polymer analogous reaction was used where PMAA or PAA reacted with disperse red 1 (DR1) via intermediate reaction of the acids and *N,N'*-dicyclohexylcarbodiimide (DCC). DCC has been used for dehydration reaction where peptides, esters or amides are formed in high conversions[10,11]. The polymer analogous reaction can avoid the radical polymerization process in which the retardation or inhibition of the polymerization occur by functional groups in the chromophore, e.g. a nitro group. The influence of residual acid remaining in the synthesized NLO polymers was also investigated.

High stability of induced polar order of the NLO polymers synthesized from PMAA can be obtained using a aminoalkyl functionalized chromophore in the synthesized NLO polymers. It is effective to introduce rigid imide structure into the poymer main-chain by heating. The imidized polymers will have imide moieties forming six-membered rings in the main-chain and can be expected to exhibit stable property of the induced polar order.

2. EXPERIMENTAL

Polymer anologous reactions of PMAA and PAA were carried out by the same procedure. Typical synthetic scheme of PMAA with DR1 as side-chain is as follows. 0.360g (1.74mmol) DCC was added to 10ml Dimethylsulfoxide (DMSO) solution of 0.30g (3.48mmol) PMAA (Dimethylformamide (DMF) for PMA). The mixture was stirred for 20min at room temperature under air. Then 0.548g (1.74mmol) DR1 was added and stirring was continued for 147hr at room temperature. The mixture was filtered by suction to remove a precipitate of urea derivative. The polymer in the resultant solution was separated by repeated reprecipitation from filtrated Tetrahydrofuran (THF) solution into water and into toluene, then by drying under reduced pressure. The chemical structure of the obtained polymer was identified by ^{1}H NMR and FT-IR spectrometer and DR1 content in the polymer was determined by elemental analysis.

A precursor polymer for NLO polymer with imide structure was prepared by two step reaction. In the first step, PMAA reacted by polymer anologous reaction with a aminoalkyl functionalized compound having electron-donating group. The second step included azo coupling reaction of the resultant polymer with aniline derivative having electron-withdrawing group.

0.360g (1.74mmol) DCC was added to 10ml DMSO solution of 0.30g (3.48mmol) PMAA. The mixture was stirred for 20min at room temperature under air. Then 0.286g (1.74mmol) of *N*-(3-aminopropyl)-*N*-methyaniline was added and stirring was continued for 1 week at room temperature. The polymers obtained were separated by the same procedure as that of the DR1 attached PMAA. The chemical structure and aminoalkyl compound content of the obtained polymer were also confirmed by the same methods as that of the DR1 attached PMAA.

0.315g (2.28mmol) *p*-nitroaniline was dissolved in a mixture containing 14ml of acetic acid and 2ml of propionic acid, and cooled to 0°C. To 3ml sulfuric acid, 0.172g (2.49mmol) sodium nitrite was then added gradually, taking care so that the temperature of the reactants was not changed. The sodium nitrite solution was added dropwise to the *p*-

nitroaniline solution, while keeping the mixture temperature at 0°C, yielding diazonium salt of *p*-nitroaniline. This solution of the diazonium salt was added to a stirred 34ml DMF solution of 0.6g PMAA that was functionalized with aminoalkyl compound (62mol% functionalized). Stirring was continued for 3 hr, while keeping the temperature at 0°C. The resulting polymer was separated by reprecipitation from DMF into acetone and by drying under reduced pressure. The introduced azo dye content was determined by ^{1}H NMR.

The imidization of this precursor polymer was concurrently done with poling process at 160°C. Imide structure was confirmed by FT-IR measurement.

NLO polymer films were prepared by dissolving them in pyridine or Dimethylacetamide (DMAc) followed by filtration. Solution was then spin-coated onto Si wafer or Indium tin oxide (ITO) coated substrates and dried for 12hr at 100°C. For second harmonic generation (SHG) experiment, chromophores in the polymer films were aligned by corona poling. For the films from DR1 functionalized PMAA and PMA, 7kV electric field was applied to the films after heating around the T_g. The films were then cooled to room temperature while the electric field was maintained. For the precursor polymer, the film was heated at 160°C to imidize it and 6.3kV voltage was applied. The second order NLO susceptibilities $\chi^{(2)}_{33}$ of the NLO polymers were measured using Maker-fringe method. A quartz crystal was used as a reference ($\chi^{(2)}_{33}$ = 0.64 pm/V). They were measured at 1.3μm fundamental wavelength from a BBO optical parametric oscillator (OPO) which is pumped by the 532nm second harmonic of the Nd:YAG laser.

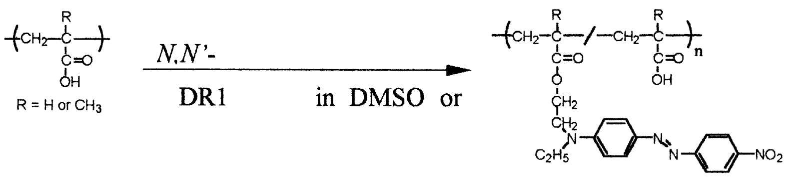

FIGURE 1. Syntheses of NLO polymers from PMAA and PAA

3. RESULTS AND DISCUSSION

3.1 syntheses of Dr1 functionalized polymers

Synthetic scheme of DR1 functionalized polymers are shown in Figure 1. The reaction using DCC resulted in high chromophore contents.

Synthesized polymers are listed in Table 1. By increasing the feed molar ratio of chromophore and reaction time, the chromophore content in the polymers increased. Contents of 45mol% was obtained for PAA which was higher than for PMAA of 29mol%. Methyl groups in the main-chain of PMAA retardates the reaction rate compared to PAA. Although the reaction solvent was not distilled prior to use in this case, higher content can be expected by using distilled solvents.

Table 1. Synthesized polymers and their glass transition

Entry	R[a)]	Time[b)] (h)	DR feed (mol%)	DR content[c] (mol%)	T_g[d)] (°C)
1	H	45	50	29	-*
2	H	49	100	45	97
3	H	93	50	39	-*
4	H	126	50	39	125
5	H	142	50	39	-*
6	CH_3	147	50	29	150
7	CH_3	100	200	15	170

a) Alkyl group in main-chain. b) Reaction time. c) DR1 content in NLO polymers determined by elemental analysis d) Glass transition temperature determined by DSC. * Not measured.

T_gs of the synthesized polymers were measured by differential scanning calorimetry (DSC) and results are also given in Table 1. T_gs depend on the chromophore contents and decrease with increase of chromophore content. High T_gs of 150 and 170°C were obtained for 15mol% and 29mol% DR1 functionalized PMAA, respectively. They were higher than those of conventional DR1 functionalized PMMA. It is indicated that these high T_gs were due to hydrogen bonding between the residual carboxyl groups. At higher chromophore content, the chromophores reduce the number of the hydrogen bonding and act as plasticizers. As a result, T_gs were depressed. The strength of hydrogen bonding changes OH absorptional peak in FT-IR spectra. Stronger hydrogen bonding shifts the OH peak to longer wavelength region. The OH peak of the DR1 functionalized PAA with 21mol% and 39mol% DR1 contents were observed at lower wavelength region and overlapped with the peaks of phenyl and alkyl CH vibrations. On the other hand, the polymer with 45mol% DR1 content showed the OH peak at 3329cm^{-1} which indicates weaker hydrogen bonding resulting in the lowered T_g of 97°C.

3.2 Optical properties of dr1 functionalized polymers

UV-Vis absorption was measured for the polymer films. As shown in Fig. 2, the absorption maxima (λ_{max}) were dependent on the chromophore contents both for DR1 functionalized PAA and PMAA.

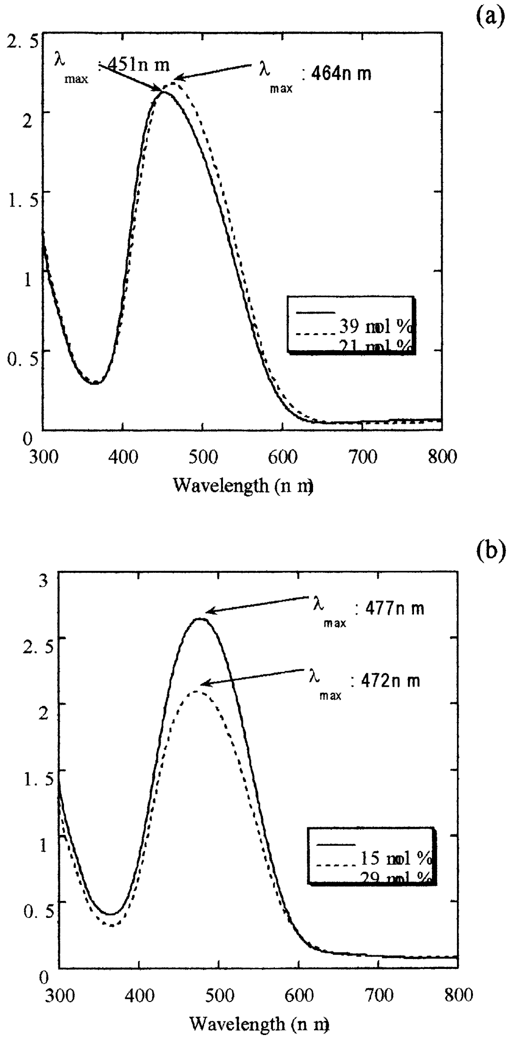

FIGURE 2. UV-Vis spectra of DR1 attached PAA (a) and PMAA (b) with different DR1 contents

The λ_{max} shifted to shorter wavelength region with increasing chromophore contents. The same results were reported and their shifts to short wavelength were assigned to an antiparallel arrangement of chromophores at higher contents[12,13]. The λ_{max} of the PAA with 21mol% DR1 was observed at shorter wavelength region relative to that from PMAA with higher chromophore content of 29mol%. Moreover, the spectra of DR1 attached PAAs were different from those of the DR1 attached PMAAs with Gaussian profile. The antiparallel chromophore arrangement easily occurred for NLO polymers from PAA.

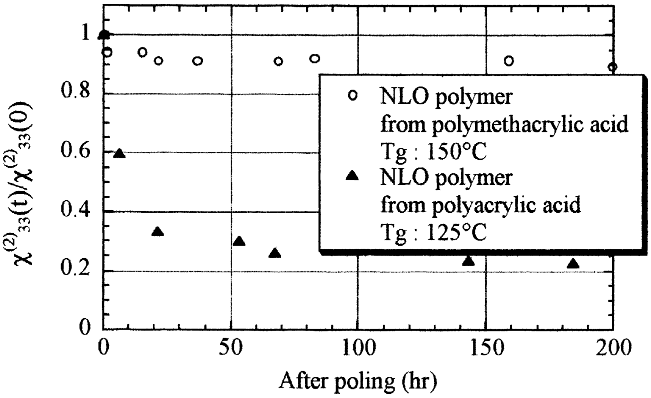

FIGURE 3. Stability of second order NLO susceptibilities at 100°C under air.

To determine $\chi^{(2)}_{33}$ values of the NLO polymers, spin-coated films were corona-poled. Maker-fringe pattern was measured using 1.3μm fundamental wave. $\chi^{(2)}_{33}$ were 48pm/V and 53pmV for NLO polymers from PAA with 39mol% DR1 content and PMAA with 29mol% DR1 content, respectively. For PAA with 45mol% DR1, optical quality was not good and SHG was not detected. The induced polar order stability of these NLO polymers was investigated at 100°C under air. After initial decrease, $\chi^{(2)}_{33}$ of PMAA with 29mol% DR1 did not change so much over a period of 200 hr, maintaining 90% of its initial value. The PAA with 39mol% DR1 showed a large decrease in $\chi^{(2)}_{33}$ to about 20% of its initial value after 200hr as shown in Figure 3.

Synthesized NLO polymers possess residual carboxyl groups. Influence of these groups on the NLO polymer was investigated by UV-Vis absorption measurement. The absorbance of the NLO polymer film from PAA with 39mol% DR1 significantly decreased after 92 days at room temperature under air. This can be attributed to hydrolysis of the

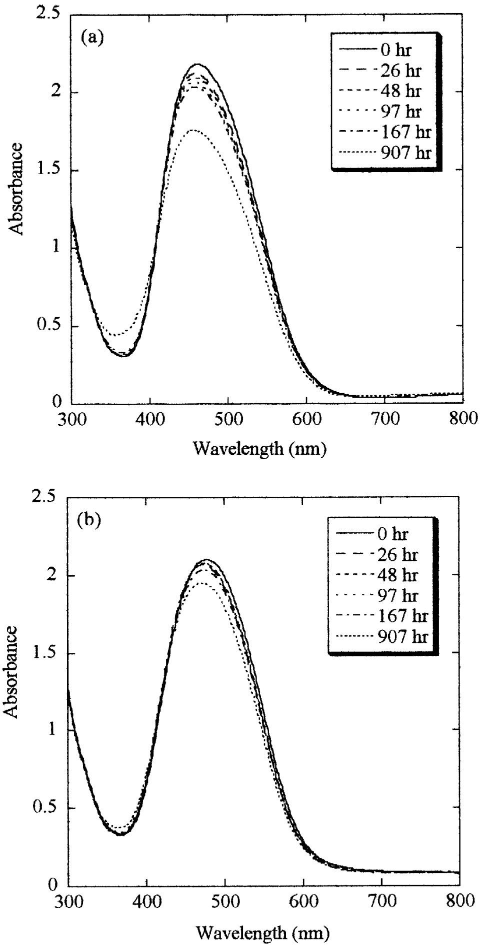

FIGURE 4. Time dependence of UV-Vis spectra of DR1 attached PAA (a) and PMAA (b) heated at 100°C

ester bonds and decomposition of chromophores by the acid of the carboxyl groups. Absorbance decreases were also detected when the NLO polymer films were kept at 100°C under air as shown in Figure 4. Absorbance decreasing rate was faster for the NLO polymer from PAA than that from PMAA. This means that hydrolysis of polyacrylate proceeds faster than that of polymethacrylate. It should be mentioned that at the elevated temperature the mechanism of the absorbance decrease includes not only hydrolysis and decomposition by the acid but also thermal decomposition of the chromophores. Thermal decomposition of chromophores occurs at lower temperature than that which was determined by thermogravimetric analysis[14].

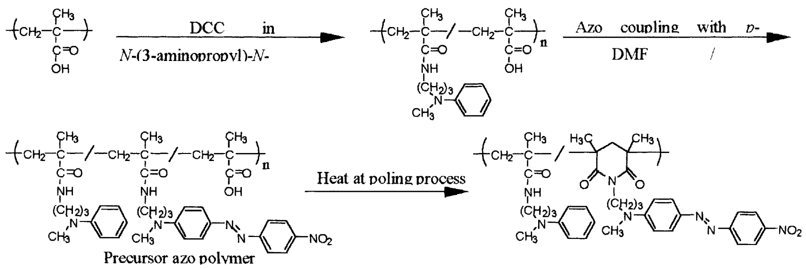

FIGURE 5. Synthesis of precursor polymer and thermal imidization

3.3 imidized polymethacrylate functionalized with aminoalkyl chromophore

A further improvement of induced polar order stability of NLO polymethacrylate was realized by introducing imide structure to the polymethacrylate. It enhances the stability when we use a chromophore with aminoalkyl moiety instead of DR1 with hydroxyethyl group. The synthesis of precursor polymer and the thermal imidization process are shown in Figure 5. Since the precursor azo polymer carries amide groups and residual carboxyl groups, heating process causes dehydration and imidization between these adjacent groups. The polymer with amide groups was synthesized using *N*-(3-aminopropyl)-*N*-methylaniline via the intermediate reaction of the acids and DCC. The functionalized molar fraction of the resultant polymer was 62mol%. Subsequently, azo groups were directly incorporated into the polymer by a post azo coupling reaction[15,16]. Azo functionalized molar fraction of 21mol% was obtained.

The precursor azo polymer film spin-coated onto an ITO substrate was imidized by heat concurrently with corona poling. The heating temperature was raised to 160°C and 6.3 kV electric field was applied. After poling for 15 min under this condition, the films were cooled to room temperature while the electric field was maintained. The cured polymer showed IR absorption at 1720cm^{-1} and 1666cm^{-1}, assigned to glutaric imide. The cured polymer possessed T_g of 165°C. The T_g was much higher than that for reported value, 132°C, for a polymethacrylate with imide structure which was imidized chemically in a solvents[17]. Cured polymer was insoluble in organic solvents. This indicates that intermolecular crosslinking reaction partially took place as well as intramolecular reaction that leads to the formation of a energetically favored six-membered ring. The poled polymer film exhibited $\chi^{(2)}_{33}$ of 45 pm/V at 1.3μm fundamental wavelength. The stability of induced polar order at 100°C under air was shown in Figure 6. $\chi^{(2)}_{33}$ value of about 90% was maintained even after 230 hr. The high stability was obtained because of the rigid imide structure and the partial crosslinking of this polymer.

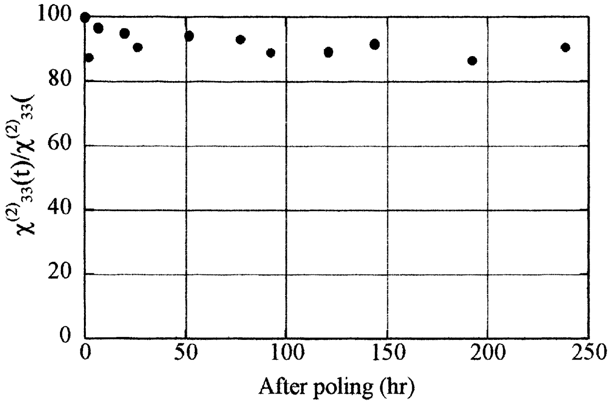

FIGURE 6. Stability of second order NLO susceptibility of a imidized polymethacrylate at 100°C under air.

CONCLUSION

Azo dye attached second order NLO polymethacrylates were synthesized from PMAA and PAA as starting materials. High chromophore contents were obtained by using DCC for the NLO polymer synthesis. Contents of 29mol% and 39mol% for PMAA and PAA were obtained. The PMAA with 29mol% DR1 showed $\chi^{(2)}_{33}$ of 53 pm/V and T_g of 150°C. The high T_g was attributed to the hydrogen bonding between residual carboxyl groups in the polymers. This polymer also exhibited high thermal stability of induced polar order at 100°C. Residual carboxyl groups in the polymers led to decrease of absorbance that indicates hydrolysis of ester bonds. By using an aminoalkyl chromophore instead of DR1 and simultaneous heating with corona poling, polymethacrylate with imide groups in the main-chain which was partially crosslinked was obtained. This cured polymer possesses T_g of 165°C and showed high thermal stability of induced polar order at 100°C under air.

REFERENCES

1. P. N. Prasad, D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules & Polymers*, J. Wiley and Sons, New York (1991)
2. M. Ahlheim and F. Lehr, "Electrooptically active polymers, 2. Influence of chromophore structure on thermal properties," *Macromol. Chem. Phys.*, **196**, pp.243-251 (1995)
3. T. Verbiest, D. M. Burland, M. C. Jurich, V. Y. Lee, R. D. Miller and W. Volksen, "Exceptionally thermally stable polyimides for second-order nonlinear optical applications," *Science*, **268**, pp.1604-1606 (1995)
4. M. Eich, B. Reck, D. Y. Yoon, C. G. Willson and G. C. Bjorklund, "Novel second-order nonlinear optical polymers via chemical cross-linking-induced vitrification under electric field," *J. Appl. Phys.* **66**, pp.3241-3247 (1989)
5. S. Marturunkakul, J. I. Chen, L. Li, R. J. Jeng, J. Kumar and S. K. Tripathy, "An interpenetrating polymer network as a stable second-order nonlinear optical material," *Chem. Mater.*, **5**, pp.592-594 (1993)
6. Z. Liang, L. R. Dalton, S. M. Garner, S. Kalluri, A. Chen and W. H. Steier, "A cross-linkable polyimide for second order optical nonlinearlities", *Chem. Mater.*, **7**, pp.941-944 (1995)
7. M. Eckl, H. Müller and P. Strohriegl, "Nonlinear optically active polymethacrylates with high glass transition temperatures," Macromo. *Chem. Phys.*, **196**, pp.315-325 (1995)
8. T. Ushiwata, E. Okamoto, K. Komatsu and T. Kaino, "Synthesis and linear and nonlinear optical properties of nonlinear optical polymers," *Polym. Prepr., Japan*, **49**, 3308 (2000)
9. Soo-Hyoung. Lee, S. Balasubramanian, D. Y. Kim, N. K. Viswanathan, S. Bian, J. Kumar and S. K. Tripathy, " Azo polymer multilayer films by electrostatic self-assembly and layer-by-layer post azo functionalization," *Macromolecules*, **33**, pp.6534-6540 (2000)

10. J. C. Sheehan and G. P. Hess, "A new method of forming peptide bonds," *J. Am. Chem. Soc.*, **77**, pp.1067-1068 (1955)
11. F. D. Greene and J. Kazan, "Preparation of Diacyl Peroxides with *N,N'*-Dicyclohexylcarbodiimide," *J. Org. Chem.*, **28**, pp.2168-2171 (1963)
12. D. Brown, A. Natansohn and P. Rochon, "Azo polymers for reversible optical storage. 5. Orientation and dipolar interactions of azobenzene side groups in copolymers and blends containing methyl methacrylate structural units," *Macromolecules*, **28**, pp.6116-6123 (1995)
13. G. Iftime, L. Fisher, A. Natansohn and P. Rochon, "photoinduced birefringence in copolymers containing Disperse Red 1 and styrene," *Can J. Chem.*, **78**, pp.409-414 (2000)
14. C. Weder, P. Neuenschwander, U. W. Suter, P. Pretre, P. Kaatz and P. Günter, "Orientational relaxation in electric-field-poled films from main-chain nonlinear optical polyamides," *Macromolecules*, **28**, pp.2377-2382 (1995)
15. M. L. Schilling, H. E. Katz and D. I. Dox, "Synthesis and reactions of cyanovinyl-substituted benzenediazonium salts for nonlinear optics," *J. Org. Chem.*, **53**, pp.5538-5540 (1988)
16. X. Wang, J. Kumar, and S. K. Tripathy, "Epoxy-based nonlinear optical polymers from post azo coupling reaction," *Macromolecules*, **30**, pp.219-225 (1997)
17. M. Ahlheim and F. Lehr, "Electrooptically active polymers. Non-linear optical polymers prepared from maleic anhydride copolymers by polymer analogous reactions," *Macromol. Chem. Phys.*, **195**, pp.361-373 (1994)