Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2011, **21**, 75–76

Mendeleev Communications

Nonlinear-optical properties of epoxyamine-based thin films

Tatyana A. Vakhonina,[a] Sirina M. Sharipova,[a] Natalia V. Ivanova,[a] Olga D. Fominykh,[a] Nikolai N. Smirnov,[b] Alexander V. Yakimansky,[b] Marina Yu. Balakina*[a] and Oleg G. Sinyashin[a]

[a] *A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Centre of the Russian Academy of Sciences, 420088 Kazan, Russian Federation. Fax: +7 843 273 7253; e-mail: mbalakina@yandex.ru*

[b] *Institute of Macromolecular Compounds, Russian Academy of Sciences, 199004 St. Petersburg, Russian Federation. Fax: +7 812 328 6869; e-mail: yak@yahoo.com*

DOI: 10.1016/j.mencom.2011.03.004

The nonlinear optical coefficients d_{33} of epoxyamine-based thin films containing 4-amino-4′-nitroazobenzene chromophore fragments in the main chain were measured by a second harmonic generation technique.

The potential applications of nonlinear-optical (NLO) polymer materials in photonics and optoelectronics are of interest.[1–3] To study the quadratic NLO activity, the polymer material is converted into the electret state with ‘frozen-in’ macroscopic polarization provided by the orientation of organic chromophore groups (the molecular sources of the effect) by an applied electric field. Epoxy polymer matrices, in particular, those based on bisphenol-A, have been intensely used for the creation of polymers with quadratic NLO activity.[1–3] The cross-linking of polymer chains is often used to ensure the relaxation stability of the NLO response.[1–3]

Here the NLO characteristics of thin films based on the model epoxyamine oligomers with hydroxyl or methacryloyl groups (CFAO and CFMAO, respectively) containing a 4-amino-4′-nitroazobenzene NLO fragment in the main chain (Figure 1) are described.

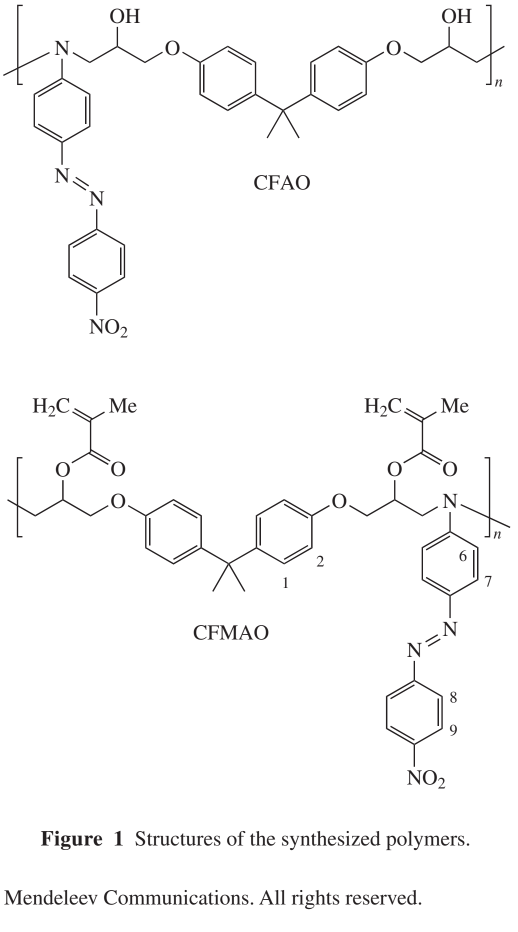

Figure 1 Structures of the synthesized polymers.

The synthesis of CFAO was carried out according to a published procedure.[4] Contrary to the techniques described in refs. 5,6, the azo-coupling reaction in a neutral organic solvent allowed us to avoid the removal of ionic admixtures from the oligomer; the presence of the admixtures results in decreasing the NLO activity. The used procedure allowed one not to subject the azo chromophore to rather severe conditions of polymerization and to obtain high-molecular-weight compounds ($M_w = 24200$, $M_w/M_n = 2.12$) with a high chromophore content (41.6%) in high yields. The obtained prepolymers possess high heat stability (according to DSC, $T_g = 130\,^{\circ}\mathrm{C}$). The interaction between the OH groups of CFAO and 4,4′-diphenylmethanediisocyanate (MDI) proceeds under mild conditions with the quantitative yield of a gel fraction and results in the formation of cross-linked polymers with T_g of about 150 °C. To avoid the problems caused by the diisocyanate moisture instability, the methacrylation of CFAO has been carried out, which afforded self-hardening polymers (CFMAO). Such reactions proceed both in the presence of catalysts[7,8] and without them.[9] It was shown by ^{1}H NMR spectroscopy that the reaction between the OH groups of CFAO [Figure 2(*a*)] and methacryloyl chloride occurs without a catalyst[9] in the presence of triethylamine only by 30% [Figure 2(*b*)]: the spectrum contains both hydroxyl proton signals and signals from the protons at C=C bonds. The use of *N*,*N*-dimethylaminopyridine as a catalyst in this reaction provided complete methacrylation: the signals of the OH-group protons completely vanish, while the intensity of the methacryloyl

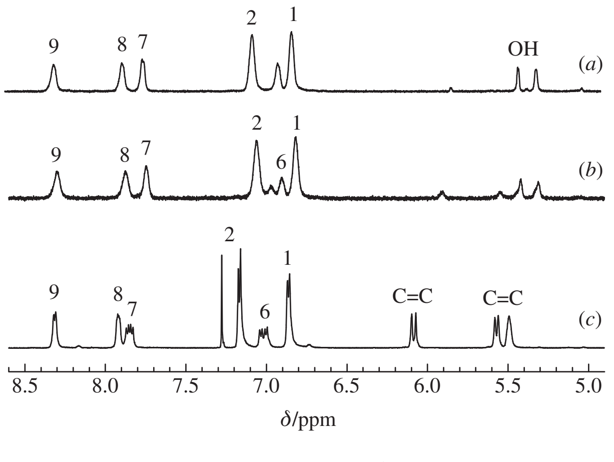

Figure 2 Fragments of a low-field region of ^{1}H NMR spectra of polymers: (*a*) CFAO in DMSO-d_6, (*b*) CFMAO obtained without a catalyst, in DMSO-d_6, (*c*) CFMAO obtained in the presence of the catalyst, in CDCl$_3$.

proton signals increases [Figure 2(*c*)]. The proton signals of the diglycidyl ether aromatic rings (δH_1, δH_2) and azo chromophores (δH_6–H_9) remained almost unchanged. The UV spectra of the polymers in THF solutions showed the hypsochromic shift of azochromophore fragment absorption band: λ_{max} = 480 (CFAO) or 457 nm (CFMAO). The synthesized long-chain CFMAO prepolymers possess high heat resistance and thermal stability ($T_{5\%}$ ~ 270 °C and T_g ~ 110 °C, respectively), as well as good film-forming properties.

Polymer films are casted on glass plates from a 7% polymer solution in cyclohexanone by a spin-coating procedure (~5000 rpm for 60–90 s). The kinetics of film cross-linking was studied by IR spectroscopy at the temperatures of solvent elimination and film drying.

The hardening process was controlled by the change in absorption intensity of the isocyanate group and the appearance of the absorption band corresponding to the stretching vibrations of the carbonyl group. The cross-linking is determined to start already at room temperature and proceeds by 20% in 4 h. On further heating of the film at 50 °C for 2 h, the reaction is accomplished by 70%. Thus, to keep the mobility of chromophore groups providing their orientation in an electric field, the CFAO + MDI films should be dried in a vacuum desiccator at room temperature during several hours. As for the CFMAO film, no cross-linking occurs under the drying conditions (16 h at 20 °C and 2 h at 50 °C). In these films, the fixation of the poling-induced order of chromophore groups obtained during poling should proceed under heating up to 160 °C, as at this temperature the cross-linking of a polymer matrix takes place.

The poling of the polymer films was carried out in a corona field at 6.5–7 kV; the distance from the tungsten needle electrode to the film surface was 1 cm. The samples were previously heated for 20 min at 110–120 °C; the poling temperature (T_p) was 110–120 °C and the poling time was ~20 min; the field was switched off after the samples were cooled to room temperature. For a number of CFAO + MDI and CFMAO samples, the poling protocol was amended with the account of cross-linking kinetics data obtained by IR spectroscopy. The poling effectiveness was controlled by UV spectroscopy on the basis of changes in the polymer film absorbance intensity before and after poling. The estimated order parameter for the test samples varies in the range of 0.2–0.36.

Polymer NLO properties were studied by a second harmonic generation technique (SHG) on an automated unit with an α-quartz (x-shear) plate as a standard; the fundamental beam was provided by a pulse Nd^{3+}:YAG laser (λ = 1064 nm; pulse duration, 15 ns; power density at the sample, 10 kW cm^{-2}). The SHG coefficients d_{ij} were obtained from the best fit of the calculated angular dependences of SHG intensities to the experimental data. In the calculations of angular dependences the internal symmetry, thickness, refraction index and film absorption were taken into account.

Table 1 Thickness (*h*) and SHG coefficients (d_{33}) of the studied polymer films.

Polymer	Sample	*h*/nm	d_{33}/pm V^{-1}
CFAO	1	390	28.9
	2	260	62.0
CFAO + MDI	3	210	28.8
	4	190	41.0
CFMAO	5	200	21.3
	6	230	12.6

The measured SHG coefficients d_{33} (Table 1) are in good agreement with the available data for related epoxyamine polymers with azochromophores in the main chain.[1,3] Thus, the poling efficiency is affected essentially by the poling protocol, as well as the procedure of film preparation. This suggestion particularly concerns molecular systems in which net formation occurs simultaneously with the poling, as in the case of samples 3 and 4. On the preparation of sample 3 in the course of drying at 50 °C, the partial curing occurred to result in a mobility loss of the chromophore fragments and corresponding reduction of the order parameter and the d_{33} value. A similar poling protocol was used for sample 4, but the application of a more adequate film preparation procedure allowed us to achieve good poling quality (the order parameter of about 0.28) and better value of d_{33} (41 pm V^{-1}).

The poling of CFMAO films was carried out at T_p = 110 °C; however, the poling procedure was different: in the case of sample 5, the field was switched on just when T_p was reached, whereas sample 6 was exposed at this temperature for 15 min before the field was switched on. The curing of a polymer matrix seems to start at the exposure of the sample at an elevated temperature thus hindering the effective chromophores alignment and resulting in a decrease in d_{33}. In the course of poling of sample 6 after a 30 min exposure at T_p, the temperature was increased up to 160 °C in order to fix the achieved poling-induced order by the curing of a polymer matrix. To make a final conclusion on the efficiency of this procedure, it is necessary to perform relaxation measurements.

This work was supported by the Russian Foundation for Basic Research (project nos. 08-03-01108-a and 09-03-00696-a).

References

1 D. M. Burland, R. D. Miller and C. A. Walsh, *Chem. Rev.*, 1994, **94**, 31.

2 A. V. Vannikov, A. D. Grishina, R. W. Rychwalski and A. T. Ponomarenko, *Usp. Khim.*, 1998, **67**, 507 (*Russ. Chem. Rev*., 1998, **67**, 451).

3 Z. Liang, Z. Yang, S. Sun, B. Wu, L. R. Dalton, S. M. Garner, S. Kalluri, A. Chen and W. H. Steier, *Chem. Mater*., 1996, **8**, 2681.

4 S. V. Shulyndin, T. A. Vakhonina, N. V. Ivanova, E. F. Gubanov, A. N. Ustyugov, O. D. Fominykh, G. A. Estrina, B. A. Rozenberg and M. B. Zuev, *Vysokomol. Soedin.*, 2005, **47**, 1438 (*Polym. Sci., Ser. A*, 2005, **47**, 808).

5 X. Wang, J. I. Chen, S. Marturunkakul, L. Li, J. Kumar and S. K. Tripathy, *Chem. Mater*., 1997, **9**, 45.

6 Hong Ma, Ju-Quan Shen, Ping Chen, Jong-Mei Wang and Ji-Ben Meng, *Eur. Polym. J.*, 1998, **34**, 1125.

7 L. Angiolini, D. Caretti, L. Giorgini and T. Salatelli, *Polymer*, 2001, **42**, 4005.

8 R. J. Jeng, Y. M. Chen, J. Kumar and S. K. Tripathy, *Pure Appl. Chem.*, 1992, **A29**, 1115.

9 H. Takase, A. Natansohn and P. Rochon, *J. Polym. Sci., Polym. Phys*., 2001, **39**, 1686.

Received: 5th July 2010; Com. 10/3556