Polyamidoimides with side chromophoric groups

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A new method was elaborated for the introduction of chromophores into the side chains of polymers by esterification of polyamidoimides containing side carboxy groups with glycidyl ethers of dyes, 4-(4-nitrophenylazo)phenol and 4-(6-nitrobenzothiazol-2-ylazo)phenol. The optimum modification conditions were found that made it possible to esterify 15, 30, 50, and 90% of the carboxy groups. The synthesized polymers possess valuable physicomechanical properties (E = 2.8 - 3.3 GPa, $\sigma_u = 69 - 90$ MPa, $\varepsilon_u = 38 - 77\%$) and glass transition temperatures of 115–125 °C, depending on the degree of esterification. After chromophore orientation in the corona discharge, all the polymers demonstrate nonlinear optical properties of the second order.

Key words: polymers, chromophores, nonlinear optics.

The creation of polymers with nonlinear optical properties is an urgent task of the modern polymer chemistry, because these materials play the key role in solution of the problem of the interaction of laser radiation with the matter, which changes the characteristics of the incident laser radiation.¹ Two main schemes for the synthesis of polymers with side chromophoric groups are presently used: (1) synthesis of polymers with side reactive groups (for instance, with carboxy, amino, or hydroxy groups) followed by modification²; (2) synthesis of monomers containing chromophoric groups and their conversion into polymers.³

In both cases, researchers face some difficulties. In the former case, the problems are related to usually low rates and degrees of polymer modification. As for the latter approach, the synthesis of chromophore-containing monomers is a rather difficult problem.

In the framework of the former approach, we developed a new method for the introduction of chromophores into the side chains of polymers by esterification of polymers containing side carboxy groups with glycidyl ethers of dyes. Polyamidoimides (PAI) were chosen as the polymeric matrices. These polymers find wide use in microelectronics due to their solubility in amide solvents and fairly good physicomechanical, thermophysical, and dielectric properties.^{4,5} The most popular method for the synthesis of PAI is the reaction of imidodicarboxylic acid dichlorides with aromatic diamines.⁶ In the present work, we synthesized PAI from 3,5-diaminobenzoic acid and di(trimellitimidic acid) dichloride with a hexamethylene bridge. The use of 3,5-diaminobenzoic acid as a monomer allows one to modify the polymer synthesized. The epoxy group is known to be highly reactive and reacts easily with the carboxy group to form an ester bond. The purpose of the present work is to synthesize PAI and glycidyl ethers of azo dyes and to study the process of modification of PAI with these glycidyl ethers and the properties of the synthesized polymers.

Results and Discussion

The starting carboxyl-containing polymer PAI was synthesized according to Scheme 1 and modified using the reaction with glycidyl ethers of azo dyes. The choice of dyes for the polymeric matrix modification is determined by the following requirements: the required compound should contain the donor and acceptor groups linked through a conjugation chain and the absorption maxima of the chromophores should be in the wavelength region not shorter than 300 nm. In addition, the molecule should contain a reactive hydroxy group. Dyes **1** and **2** containing the hydroxy group meet these requirements. They were synthesized by the azocoupling reaction (Scheme 2).

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 6, pp. 1438–1444, June, 2005. 1066-5285/05/5406-1481 © 2005 Springer Science+Business Media, Inc. Scheme 1







Glycidyl ethers of the synthesized dyes should be prepared in the next stage. Such ethers are known to be the most convenient for the modification of polymers containing carboxy groups in the side chains. The synthesis of glycidyl ethers is usually rather difficult. As a rule, they are prepared by ring closure in a strongly alkaline medium at high temperatures. In our case, this approach is inappropriate, because azo compounds are unstable in concentrated alkalis. Therefore, we developed a new method for the synthesis consisting of the reaction of hydroxylcontaining dyes with epichlorohydrin in the presence of a catalyst (katamine). This method allows the reaction to be carried out under mild conditions to form ethers 3and 4 in high yields (Scheme 3).





The reaction of α -oxide compounds with carboxylic acids has been known long ago (see, *e.g.*, Ref. 7). The synthesized glycidyl ethers reacted with the carboxy groups of PAI in the presence of a catalyst, *viz.*, dimethylbenzylamine (DMBA) or dicyclohexyl peroxydicarbonate (CPC), in *N*-methylpyrrolidone (NMP). For a strong nonlinear optical response it is sufficient that the degree of modification of the polymer with side chromophoric groups was 50%. This value was chosen as a reference for selecting modification conditions. Our studies showed that the use of more than twofold molar excess of the glycidyl

Т	3 : COOH*	Cata- lyst	Degree of modification after <i>t</i> **/h						
/°C			2	4	6	12	18	24	30
40	2:1	DMBA	_	_	4.8	_	13.3	29.5	33.3
60	2:1	DMBA	25.7	29.5	40.0	63.8	74.3	84.8	89.5
80	2:1	DMBA	30.5	44.7	66.6	89.0	90.0	_	_
60	1:1	DMBA	4.8	25.7	25.7	36.2	38.1	40.9	58.1
40	2:1	CPC	14.3	14.3	14.3	—	—	—	—

Table 1. Degree of modification of PAI with chromophore 3 under different reaction conditions

* Molar ratio (relative to the COOH groups of the polymeric PAI chain).

** Duration of esterification.

ether of the azo dye with respect to the content of carboxy groups in the polymer or more than 3% of the catalyst relative to the PAI weight does not increase substantially the degree of esterification. In this case, the reaction temperature and its duration are the determining parameters (Table 1). The use of a twofold excess of a glycidyl ether (**3** or **4**) with respect to the carboxyl-containing PAI, DMBA as a catalyst, and 60 °C were the optimum conditions for PAI modification (see Table 1). The modification of PAI is depicted in Scheme 4.

According to the data from UV spectroscopy, the spectra of glycidyl ethers of azo dyes **3** and **4** have absorption maxima at $\lambda_{max} = 370$ and 420 nm, respectively (Fig. 1). No considerable shift of the absorption maximum was observed after the reaction of compound **3** with the polymer (Fig. 2), which indicates the complete retention of the chromophore structure after its introduction into the side chain of the polymer.

All further mechanical, thermochemical, and thermogravimetric studies were carried out for PAI samples modified with glycidyl ether **3** (PAI-1).

Thermal stability of polymers with side chromophoric groups is one of the most important characteristics. Thermogravimetric data make it possible to estimate boundaries of thermal stability of the synthesized materials. The TGA data for the prepared dyes and PAI-1 with a modification degree of 50% are given in Table 2.

As follows from the data in Table 2, the starting PAI possesses rather high thermal stability typical of this class of polymers: the temperature of the onset of its thermal destruction is above 300 °C. Azo dye 1 is noticeably inferior to PAI in its thermal stability. At the same time, the thermal stability of PAI-1 is similar to that of the starting polymer and even somewhat greater. Most likely, the polymeric environment of the dye introduced into PAI enhances its thermal stability.

Scheme 4





500

 λ/nm

Fig. 1. UV spectra of chromophores 3(1) and 4(2).

400

300

0.4

0.3

0.2

0.1



Fig. 2. UV spectra of the original PAI (1) and PAI-1 with a degree of modification of 30% (2).

Table 2. Thermal stability of the synthesized chromophores and polymers

Com-	τ_1	τ_5	τ_{10}		
pound	°C				
1	258	290	297		
PAI	333	358	377		
PAI-1	341	370	397		

Note. τ_1 , τ_5 , and τ_{10} are the temperatures at which the mass losses of the sample upon heating were 1, 5, and 10%, respectively.

Studies of the mechanical and thermomechanical properties of the synthesized polymers are required to make final conclusion about a possibility of their usage. The polymers used in optical devices should possess rather high strength in addition to necessary optical characteristics, because these materials can undergo mechanical loads during exploitation. Studies of the thermomechanical

Table 3. Mechanical characteristics (Young's modulus (*E*), ultimate tensile strength (σ_u), and ultimate tensile strain (ε_u)) and glass transition temperatures (T_g) of the PAI-1 films at different contents of chromophoric groups (α)

α (%)	<i>E</i> /GPa	σ_u/MPa	ε _u (%)	$T_{\rm g}/^{\circ}{ m C}$
0	2.80	75	38	116
15	3.06	86	45	123
30	2.78	74	40	123
50	3.32	87	77	123
90	2.77	74	51	124

properties of the polymers would allow one to determine the temperature range of exploitation of articles based on them and to choose optimum conditions for orientation of side chromophoric groups in an electric field (the socalled poling), which occurs at temperatures close to the glass transition temperature of the polymer. The main mechanical characteristics and glass transition temperatures (T_g) of the starting and modified polymers with different degrees of esterification (α) are given in Table 3.

As can be seen from the data in Table 3, films of all the synthesized polymers have high mechanical strength. High values of Young's modulus of the polymers indicate strong intermolecular interactions in them. It is noteworthy that the character of plots of the mechanical characteristics vs. degree of modification of the starting polymer is extreme: the maximum values of all parameters are observed for the films of esterified PAI with $\alpha = 50\%$. This suggests that the side chains can play an ordering role in polymer structure formation when their concentration is not too high and creates no hindrance for mutual packing.

The thermomechanical curves of the films of all the modified polymers demonstrate two pronounced transitions: at low temperature (120-125 °C), which reflects the process of material softening, and at high temperature (225–240 °C). The nature of the latter is being refined. However, we can assume at present that this transition indicates that the material contains ordered structures. The data of thermomechanical measurements were confirmed by the results of optical dilatometry. On the whole, the data from thermomechanics and dilatometry suggest a complex character of thermorelaxation processes in the materials under study. Finally, a comparison of the results of thermomechanical studies and TGA (see Tables 2 and 3) suggests that the thermal characteristics of the materials favor the orientation of the side groups near the glass transition temperature: the segmental mobility is disinhibited at comparatively low temperatures, which lie much lower than the range of the onset of thermodestruction of the material.

In the final stage of the work, we studied the nonlinear optical properties of the modified polymers after they were polarized in a corona discharge field. The intensity of second harmonic generation in the polymeric films was compared with that in a quartz crystal $(d_{11} = 0.45 \text{ Pm V}^{-1}).^8$

The nonlinear optical coefficients (d_{eff}) for the polymer modified with chromophore **3** are 2.7, 3.3, 4.7, and 7.6 Pm V⁻¹ at the degrees of substitution of 15, 30, 50, and 90%, respectively, and remain almost unchanged for one month. The d_{eff} value for PAI-2 with a degree of modification of 20% was 2.0 Pm V⁻¹, *i.e.*, somewhat lower than that for PAI-1 with the same degree of modification. At the same time, the PM3 quantum-chemical calculation predicts⁹ a 1.6-fold higher molecular square nonlinearity for chromophore **4** than that for **3** ($\beta = 27 \cdot 10^{-30}$ and $16.6 \cdot 10^{-30}$ esu, respectively). It can be assumed that considerably higher orientation of the side chromophoric groups can be achieved in corona for the films of the polymer modified with chromophore **4**.

Thus, the method for esterification of polymers containing side carboxy groups with glycidyl ethers of dyes was developed. The method provides wide potential for introduction of chromophoric groups into the side chains of polymers. The results obtained are significant for preparing systems with nonlinear optical properties.

Experimental

N-Methylpyrrolidone and DMF were dried with CaH₂ and distilled *in vacuo*. Thionyl chloride and acetic anhydride were distilled, collecting fractions with b.p. 75.5–77 and 139–140 °C, respectively. Pyridine was dried with granulated KOH and distilled, collecting a fraction with b.p. 114–115 °C. 3,5-Diaminobenzoic acid, CPC, and DMBA were purified using a known procedure.¹⁰ Katamine (AB trade mark, Me(CH₂)_nN⁺Me₂BnCl⁻; n = 8-16) was used as a 52% aqueous solution without additional purification. 2-Aminobenzothiazole (97% purity) and trimellitic anhydride (99% purity, Aldrich) were used as received. 1,6-Hexamethylenediamine was distilled *in vacuo* (m.p. 43 °C).

The degree of substitution of carboxy groups was determined by potentiometric titration of solutions of precipitated samples of the esterified polymers in DMF with a 0.08 M aqueous solution of KOH.

Films for physical studies were prepared from solutions of the respective polymers by casting onto glass plates using a template followed by vacuum drying in a stepwise temperature—time mode (final temperature 100 °C) to a constant mass. The film thickness was $30-40 \ \mu m$.

UV spectra of films were measured on a Specord UV-VIS instrument in the 200–500 nm interval using a commercial system (Casper Instr. Co) with a 350-W mercury lamp as a source. ¹H NMR spectra of 1% solutions were obtained on a Bruker AC-200 spectrometer (200 MHz) with Me₄Si as an internal standard.

Mechanical tests of the films, where Young's modulus (*E*), ultimate tensile strength (σ_u), and ultimate tensile strain (ε_u) were determined, were carried out with a UTS 10 universal

technique (UTStestsysteme, Germany) in a uniaxial extension mode.

Thermogravimetric analyses of the chromophores and polymers were carried out on a laboratory thermobalance, constructed on the basis of ADB-200 laboratory analytical balances, in a self-generated atmosphere with a rate of temperature increase of 5 deg min⁻¹. The sample mass was 50 mg. The temperatures at which mass losses of the sample during heating reached 1, 5, and 10% (τ_1 , τ_5 , and τ_{10} , respectively) were determined from the results of the tests.

Glass transition temperatures were determined by the thermomechanical method on a UMIV-3 instrument with the load $\sigma \le 0.5$ MPa on the sample.

Studies on the nonlinear optical properties were carried out with samples of films with the thickness from 1.5 to 2.5 μ m prepared by centrifugation on cover glass plates 180 μ m thick. The samples were dried *in vacuo* for 2 days at 50 °C. The samples were polarized in a corona discharge field. The distance from the tungsten needle electrode to the sample was 1 cm and the corona discharge voltage was 6 kV. The current through the sample did not exceed 2 μ A.

The nonlinear optical properties of samples were studied by recording the intensity of second harmonic generation under YAG-Nd³⁺ laser pulse irradiation. The wavelength of the incident radiation was 1.06 μ m, and the pulse duration was 15 ns. The efficiency of second harmonic generation was characterized by the nonlinear optical coefficient of the film (d_{eff}).

N,N'-Hexamethylenedi(trimellitimidic acid). A solution of trimellitic anhydride (49 g, 0.25 mol) in DMF (250 mL) with a temperature not exceeding 10 °C was added with stirring to a solution of 1,6-hexamethylenediamine (14.8 g, 0.13 mol) in DMF (120 mL) at 0 °C under argon. The mixture was stirred for 6 h at ~20 °C, then freshly distilled Ac₂O (30.5 mL, 0.32 mol) and pyridine (7.5 mL, 0.093 mol) were added, and the resulting solution was refluxed for 6 h. This resulted in a yellow solution, which yielded white crystals of *N*,*N'*-hexamethylenedi(trimellitimidic acid) after ~12 h at ~20 °C. The precipitate was filtered off, washed with acetone and ether, and dried. The yield was 33.5 g (56.5%).

N,N⁻**Hexamethylenedi(trimellitimidic acid) dichloride.** The acid obtained (15 g, 0.032 mol) was refluxed for 10 h with SOCl₂ (120 mL). After cooling to ~20 °C, a white precipitate that formed was filtered, thoroughly pressed on a filter, and dried in air for 40 min. The yield of the target acid chloride was 8.5 g (52%), m.p. 169–171 °C. Found (%): C, 57.52; H, 3.61; N, 5.58; O, 19.12. $C_{24}H_{18}Cl_2N_2O_6$. Calculated (%): C, 57.49; H, 3.59; N, 5.59; O, 19.16.

Synthesis of PAI (*cf.* Ref. 6). *N*,*N*[']-Hexamethylenedi(trimellitimidic acid) dichloride (4.4485 g, 0.00887 mol) was added with stirring to a solution of 3,5-diaminobenzoic acid (1.31 g, 0.0086 mol) in NMP (28.5 mL) at -10 °C. The mixture was stirred for 30 min, after which cooling was discontinued. After 20 min, propylene oxide (1 mL) was added, and stirring was continued for 4 h at ~20 °C. If the solution was very viscous, it was diluted with NMP to a 10% concentration. The resulting solution of the polymer was poured as a thin stream into 1 L of water with permanent stirring. Polymer fibers were filtered off, washed with acetone, and dried *in vacuo* for 24 h at 50 °C. The yield was 90%. Found (%): C, 64.14; H, 4.14; N, 9.65; O, 22.07. C₃₁H₂₄N₄O₈. Calculated (%): C, 64.12; H, 4.16; N, 9.61; O, 22.11. ¹H NMR (DMSO-d₆), δ : 1.35 (s, 4 H, H(3'), H(4')); 1.62 (s, 4 H, H(2'), H(5')); 3.60 (m, 4 H, H(1'), H(6')); 7.95 (d, 2 H, H(5), *J* = 7.9 Hz); 8.16 (s, 2 H, H(3)); 8.42 (d, 2 H, H(6), *J* = 7.9 Hz); 8.52 (s, 2 H, H(2")); 8.71 (s, 1 H, H(4")); 10.73 (s, 2 H, NH).

4-(4-Nitrophenylazo)phenol (1) and 4-(6-nitrobenzo-thiazol-2-ylazo)phenol (2) were synthesized according to a known procedure.¹¹

4-(4-Nitrophenylazo)phenol (1). A mixture of *p*-nitroaniline (20 g, 0.15 mol), concentrated HCl (51 mL), and water (87 mL) was heated with stirring to 70 °C, the solution was cooled to ~20 °C, more water (145 mL) was added, and the resulting mixture was cooled to -8 °C. A solution of NaNO₂ (12.2 g, 0.177 mol) in water (28.5 mL) was cooled to 5 °C and poured into a suspension of *p*-nitroaniline. Diazonium chloride is formed with heat evolution and temperature should not exceed 5 °C. The suspension gradually transformed into a solution. After 30 min, an emulsion of phenol was poured to this solution of diazonium chloride, maintaining temperature not higher than 0 °C (the emulsion was prepared as follows: phenol (14.5 g, 0.154 mol) was dissolved on heating in water (145 mL), and the mixture was cooled to ~20 °C). Then, a solution of Na_2CO_3 (54.3 g, 0.51 mol) in water (220 mL) was added to the reaction mixture. The resulting suspension was stirred for 2 h, maintaining the temperature at a level not higher than 10 °C. Then the suspension was diluted with equal volume of water, heated to 50-60 °C with continuous stirring, cooled to 40 °C, and acidified with hydrochloric acid to pH 5-6. The resulting brown precipitate was filtered off, washed with large amount of water, and thoroughly pressed. The product was recrystallized from glacial AcOH. The yield was 29.5 g (84%), m.p. 213–214 °C. Found (%): C, 59.45; H, 3.67; N, 17.31; O, 19.57. C₁₂H₉N₃O₃. Calculated (%): C, 59.26; H, 3.73; N, 17.28; O, 19.73. ¹H NMR (DMSO-d₆), δ: 6.99 (d, 2 H, H(2), H(6), *J* = 8.4 Hz); 7.88 (d, 2 H, H(3), H(5), *J* = 8.4 Hz); 8.01 (d, 2 H, H(2'), H(6'), *J* = 9.3 Hz); 8.37 (d, 2 H, H(3'), H(5'), *J* = 9.3 Hz); 10.68 (s, 1 H, OH).

4-(6-Nitrobenzothiazol-2-ylazo)phenol (2). Glacial AcOH (35 mL) and a solution of 2-aminobenzothiazole (5.1 g, 0.026 mol) in glacial AcOH (150 mL) were added to a solution of NaNO₂ (1.98 g, 0.028 mol) in concentrated H_2SO_4 (30 mL) at 10-12 °C. The suspension was stirred for 20 min at 12 °C and poured onto crashed ice (150 g). The resulting mixture was poured with stirring into a solution of phenol (2.45 g, 0.026 mol) in 50% AcOH (50 mL) cooled to 0-5 °C. After 1 h, a red precipitate was filtered off, washed with water to neutral pH, and recrystallized from ethanol. The yield was 2.92 g (50%), m.p. 274 °C. Found (%): C, 52.04; H, 2.62; N, 18.69; O, 15.93; S, 10.73. C₁₂H₈N₄O₃S. Calculated (%): C, 52.00; H, 2.69; N, 18.66; O, 15.98; S, 10.68. ¹H NMR (DMSO-d₆), δ: 6.96 (d, 2 H, H(2), H(6), J = 8.6 Hz); 7.94 (d, 2 H, H(3), H(5), J =8.6 Hz); 8.14–8.46 (m, 2 H, H(4'), H(5')); 9.07 (s, 1 H, H(7')); 11.17 (s, 1 H, OH).

Glycidyl ethers of azo dyes were synthesized according to a described procedure.¹²

Glycidyl ether of 4-(4-nitrophenylazo)phenol (3). Sodium carbonate (3.22 g, 0.03 mol) and a 52% solution of katamine AB (32.4 mL, 0.04 mol) were added to a mixture of 4-(4-nitrophenylazo)phenol (1) (29.5 g, 0.12 mol) and epichlorohydrin (38 mL) at 55 °C followed by a 50% aqueous solution of NaOH (10.7 mL) with vigorous stirring at a temperature not exceeding 60 °C. The mixture was stirred for additional 3 h at 55–60 °C, cooled to ~20 °C, and poured into a solution of NaOH (4.85 g) and borax (23 g) in water (1210 mL). The precipitate that formed was filtered off, washed with water, dried, and purified by chromatography on a column with Al₂O₃ (eluent acetone). The yield



was 26.6 g (73%), bright orange crystals, m.p. 153–154 °C. Found (%): C, 61.64; H, 6.42; N, 12.50; O, 19.44. $C_{15}H_{13}N_3O_4$. Calculated (%): C, 61.62; H, 6.39; N, 12.68; O, 19.31. ¹H NMR (CDCl₃), & 2.79 (m, 1 H, H(5")); 2.96 (m, 1 H, H(4")); 3.40 (m, 1 H, H(3")); 4.05 (m, 1 H, H(2")); 4.87 (m, 1 H, H(1")); 7.92 (d, 2 H, H(2), H(6), J = 8.4 Hz); 7.92 (d, 2 H, H(3), H(5), J = 8.4); 7.99 (d, 2 H, H(2'), H(6'), J = 9.3 Hz); 8.35 (d, 2 H, H(3'), H(5'), J = 9.3 Hz).

Glycidyl ether of 4-(6-nitrobenzothiazol-2-ylazo)phenol (4) was synthesized similarly from phenol **2**. The yield was 52%, reddish-brown crystals, m.p. 160 °C. Found (%): C, 55.59; H, 5.23; N, 14.40; O, 16.44; S, 8.34. $C_{15}H_{12}N_4O_4S$. Calculated (%): C, 55.66; H, 5.19; N, 14.42; O, 16.48; S, 8.25. ¹H NMR (DMSO-d₆), 8: 2.72–2.97 (m, 1 H, H(5")); 3.32–3.50 (m, 1 H, H(4")); 3.64–3.89 (m, 1 H, H(3")); 4.14–4.64 (m, 2 H, H(1"), H(2")); 6.48 (d, 2 H, H(2), H(6), *J* = 8.6 Hz); 7.56 (d, 2 H, H(3), H(5), *J* = 8.6 Hz); 8.08 (d, 1 H, H(4'), *J* = 8.5 Hz); 8.30 (d, 1 H, H(5''), *J* = 8.5 Hz); 8.77 (s, 1 H, H(7')).

PAI was modified with glycidyl ethers of azo dyes according to a known procedure.¹⁰

Modification of PAI with glycidyl ether 3. Glycidyl ether of 4-(4-nitrophenylazo)phenol (3) (4.85 g, 0.016 mol) and DMBA (0.145 g, 0.0011 mol, 3% of the chromophore mass) were added with stirring to a solution of PAI (4.7 g, 0.008 mol) in NMP (180 mL) at 60 °C. The reaction mixture was stirred for 2-30 h at 60 °C (see Table 1). The modified polymer was isolated by precipitation with water. The precipitated polymer was filtered off and dried, and unconsumed chromophore was extracted with acetone in a Soxhlet apparatus for 48 h. PAI-1 was obtained. <u>*n* : *m* = 15 : 85</u>. Found (%): C, 63.89; H, 4.21; N, 9.93; O, 21.97. $(C_{46}H_{38}N_7O_{12})_{0.15}(C_{31}H_{24}N_4O_8)_{0.85}$. Calculated (%): C, 63.84; H, 4.17; N, 9.97; O, 22.02. <u>*n* : *m* = 30 : 70</u>. Found (%): C, 63.55; H, 4.17; N, 10.27; O, 22.01. (C₄₆H₃₈N₇O₁₂)_{0.3}(C₃₁H₂₄N₄O₈)_{0.7}. Calculated (%): C, 63.58; H, 4.21; N, 10.24; O, 21.97. <u>n: m = 50: 50</u>. Found (%): C, 63.35; H, 4.26; N, 10.51; O, 21.88. $(C_{46}H_{38}N_7O_{12})_{0.5}(C_{31}H_{24}N_4O_8)_{0.5}$. Calculated (%): C, 63.29; H, 4.24; N, 10.55; O, 21.92. <u>*n*</u> : <u>*m*</u> = 90 : 10</u>. Found (%): C, 62.79; H, 4.29; N, 11.08; O, 21.84. (C46H38N7O12)0.9(C31H24N4O8)0.1. Calculated (%): C, 62.82; H, 4.31; N, 11.04; O, 21.83. ¹H NMR (DMSO-d₆), δ: 1.35 (s, 4 H, H(12), H(13)); 1.62 (s, 4 H, H(11), H(14)); 3.60 (m, 4 H, H(10), H(15)); 3.84–4.42 (m, 5 H, H(1'), H(2'), H(3')); 7.16 (d, 2 H, H(2"), H(6"), J = 7.0 Hz); 7.95-8.70 (m, 15 H, H(1), H(2), H(3), H(7), H(8), H(9), H(4), H(5), H(6), H(3''), H(5''),H(3"), H(5"), H(2"), H(6")); 10.73 (s. 2 H, NH).

Modification of PAI with glycidyl ether 4. PAI-2 modified with chromophore **4** was obtained using a similar procedure. n : m = 20 : 80. Found (%): C, 63.02; H, 4.13; N, 10.29; O, 21.58; S, 0.98. (C₄₆H₃₈N₇O₁₂S)_{0.2}(C₃₁H₂₄N₄O₈)_{0.8}. Calculated (%): C, 63.00; H, 4.08; N, 10.32; O, 21.61; S, 0.99. ¹H NMR (DMSO-d₆), δ : 1.35 (s, 4 H, H(12), H(13)); 1.62 (s, 4 H, H(11), H(14)); 3.60 (m, 4 H, H(10), H(15)); 2.84–4.52 (m, 5 H, H(1'), H(2'), H(3')); 7.16 (d, 2 H, H(2''), H(6''), J =

7.6 Hz); 7.95–8.70 (m, 13 H, H(1), H(2), H(3), H(4), H(5), H(6), H(7), H(8), H(9), H(3"), H(5"), H(4"'), H(5"')); 9.22 (s, 1 H, H(7"')); 10.73 (s, 2 H, NH).

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