

## Influence of residual solvent on relaxation behavior of polymer films based on glycidyl derivatives of 3, 5, 7, 3',4'-pentahydroxyflavone

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Structural parameters and optical anisotropy relaxation dynamics of cross-linked polymers obtained from 7,4'-diglycidyl-, 7,3',4'-triglycidyl- and 3,7,3',4'-tetraglycidyl ethers of quercetin (3,5,7,3',4'-pentahydroxyflavone) are investigated. Values of effective cross-linked density and molecular weight between the cross-linked units, as well as dynamics of after-poling polymer relaxation were analyzed for polymer films containing residual solvent (acetone) and solvent-free annealed samples. It was found that solvent removal leads to growth of cross-linked density and to decrease of molecular weight between the cross-linked units. It was found that relaxation dynamics of polymers based on 3,7,3',4'-tetraglycidyl quercetin does not depend on the presence of residual solvent. Solvent containing polymers based on 7,4'-diglycidyl- and 7,3',4'-triglycidyl ethers of quercetin have substantially faster relaxation dynamic than corresponding annealed polymers. The mechanism of the residual solvent influence on the relaxation dynamics of polymer films has been proposed.

**Keywords:** residual solvent; polymer films; chromophore; relaxation behavior.

Исследованы структурные параметры и релаксационная динамика оптической анизотропии шитых функциональных полимеров полученных из 7,4'-диглицидилового, 7,3,4'-триглицидилового и 3,7,3',4'-тетраглицидилового эфиров кверцетина (3,5,7,3',4'-пентагидроксифлавона). Проанализированы значения эффективной плотности шивки и молекулярной массы между узлами сетки, а также динамика релаксации полимера после поляризации полимерных пленок, содержащих остаточных растворитель (ацетон) и не содержащих остаточный растворителей после отжига. Установлено, что удаление растворителя приводит к росту плотности шивки и к уменьшению молекулярной массы между узлами сетки. Показано, что динамика релаксации полимеров на основе 3,7,3',4'-тетраглицидилового эфира кверцетина не зависит от наличия остаточного растворителя. Полимеры на основе 7,4'-диглицидилового и 7,3',4'-триглицидилового эфиров кверцетина, которые содержат растворитель, имеют значительно более быструю динамику релаксации, чем закаленные образцы. Предложен механизм влияния остаточного растворителя на динамику релаксации полимерных пленок.

**Вплив залишкового розчинника на релаксаційну поведінку полімерних плівок на основі гліцидильних похідних 3, 5, 7, 3', 4'-пентагидроксифлавоноу.** *Д.Мішуров, О.Розаль, О.Бровко.*

Досліджено структурні параметри і динаміку релаксації оптичної анизотропії шитих полімерів, отриманих із 7,4'-дигліцидилового, 7,3,4'-триглицидилового- і 3,7,3', 4'-тет-

рагліцидилового етерів кверцетину (3,5,7, 3', 4'-пентагідроксифлавону). Проаналізовано значення ефективної густини зшивання і молекулярної маси між вузлами сітки, а також динаміку релаксації полімерів після поляризації полімерних плівок. Встановлено, що видалення розчинника з полімерів призводить до зростання густини зшивання і до зменшення молекулярної маси між вузлами сітки. Динаміка релаксації полімерів на основі 3,7,3',4'-тетрагліцидилового етеру кверцетину не залежить від наявності залишкового розчинника. Полімери на основі 7,4'-дигліцидилового- і 7,3', 4'-тригліцидилового етерів кверцетину, що містять залишковий розчинник, мають значно швидшу динаміку релаксації, ніж закалені зразки. Запропоновано механізм впливу залишкового розчинника на динаміку релаксації полімерних плівок.

## 1. Introduction

Polymer chromophore-containing cross-linked functional materials are widely used in various nonlinear optical (NLO) applications [1–3]. Usually, such polymers are used as thin films deposited on various solid substrates from solutions with the spin-coating technique [4, 5] in the presence of orienting electric field (poling process). Optical and other physico-chemical properties of such films change after removing the electric field because of the after-poling relaxation processes — i.e. changing positions of the chromophore fragments over time resulting in the chromophore disordering and thus causing decrease of the optical anisotropy.

Since formation of the polymer films occurs from solution, the questions about influence of the solvents on the polymer properties and about methods of the solvent removal are of high importance. Previous studies have shown that interaction of the residual solvent with the cross-linked polymers leads to changing the physico-chemical parameters of 3D networks. As it was earlier noticed, that the residual solvent is an active plasticizer [6] influencing the morphology, glass transition temperature and free volume of the polymer systems. In some cases, the antiplasticization effect and the non-Fickian diffusion were also observed [7]. It was shown that in the presence of the residual solvent, the physical and chemical properties determined by conformational set do not correspond to the properties of the pure polymer, but demonstrate the average properties of the "polymer-residual solvent" system. Finally, the residual solvent influences the relaxation behavior and temporal stability of the polymer films with nonlinear properties [8].

The action of the residual solvents on the polymers is usually described in accordance with the free volume theory [9, 10], which allows to explain the dependence of physico-chemical properties of polymer materials on packing of the polymer chains, bulk structure and microstructure of the polymers.

In previous studies, it was shown that removal of the residual solvent from the polymer films is very arduous task due to non-covalent interactions between active functional groups of the polymers and solvent molecules. The solvent removal is closely related to the conditions of formation and heat treatment of the polymer films [11].

Basically, effect of the residual solvent is considered only as a factor in determining the morphology of the polymer chains in the films. Not much attention is paid to short-scale mobility inside the elementary units, conformational composition and conformational ordering or disordering of these units.

The present work generalizes the earlier data and provides the new data concerning the interactions in the "polymer-solvent" system and the residual solvent effect on the conformational structure and physico-chemical properties of the polymer films. The new correlations experimentally observed for the polymer films and their explanations are presented in the paper.

## 2. Experimental

### 2.1 Materials

Polymer films based on described previously di-, tri- and tetraglycidyl derivatives of 3, 5, 7, 3',4'-pentahydroxyflavone (quercetin) were used [12]. Diethylene-triamine (DETA, Dow Chemical), was used as a hardener.

### 2.2 Preparation of polymer films

Glycidyl ethers of quercetin were dissolved in acetone at concentration of about 0.1 g/mL. DETA was added in stoichiometric quantities proportionally to number of glycidyl groups in the corresponding quercetin derivatives. Thereafter, thin films were spin-coated onto pre-cleaned glass microscope cover slides of 170  $\mu\text{m}$  at 1000 rpm for 0.5 min and cured at the room temperature for 24 h in vacuum. The thickness of the obtained films was 1.0  $\mu\text{m}$ .

The used glass-microscope cover slides were ultrasonically cleaned in detergent solution for about 10 min, followed by rinsing it in deionized water. These were then boiled in ethanol and dried at 90°C for 10 min.

The network segments of polymers P2GEQ, P3GEQ and P4GEQ obtained correspondingly from di-, tri- and tetraglycidyl derivatives of quercetin are depicted in Fig. 1.

### 2.3 Polymer films poling

The polymer films were poled by the corona poling technique. Poling was done simultaneously with curing reaction. Temperature of the film was increased to 200°C then the corona field was applied, and poling was carried out for 1 h. The corona current was held at 2.5  $\mu\text{A}$  with an electrode potential of 6 kV. Finally, the films were cooled to the room temperature, while the electric field was kept on.

To remove residual solvent the polymer films were then annealed for 3 h at 100°C.

### 2.4 Characterization

The presence of residual solvent in the polymer films were monitored by FTIR-ATR (attenuated total reflection) spectroscopy detecting a stretching vibration absorption band of acetone C=O group at about 1710  $\text{cm}^{-1}$ . The FTIR-ATR spectra were registered on ALPHA FT-IR Spectrometer with a diamond crystal in the range of 400–4000  $\text{cm}^{-1}$ . Resolution of 4  $\text{cm}^{-1}$  was used, and 32 scans were averaged.

Concentration of the residual solvent in the polymer films was determined with microgravimetric method. The concentration (per cent) of the residual solvent was calculated by the following equation:

$$C = \frac{W_w - W_d}{W_w} \cdot 100, \quad (1)$$

where  $C$  is concentration of residual solvent in film;  $W_w$  is wet weight of film;  $W_d$  is dry weight of film after drying to constant weight.

Structural parameters of the polymer networks were investigated by measuring molecular weights between crosslinks  $M_c$  (using the Flory-Rehner method) and crosslink densities  $\nu_c$  (using the extraction method). The latter were performed according to ASTM D 2765. It included extraction of the films in Soxhlet apparatus at 56.2°C for 24 h using acetone as solvent. The gel content was calculated as a ratio of the final weight to the initial weight of the films, as described in Eq. 2:

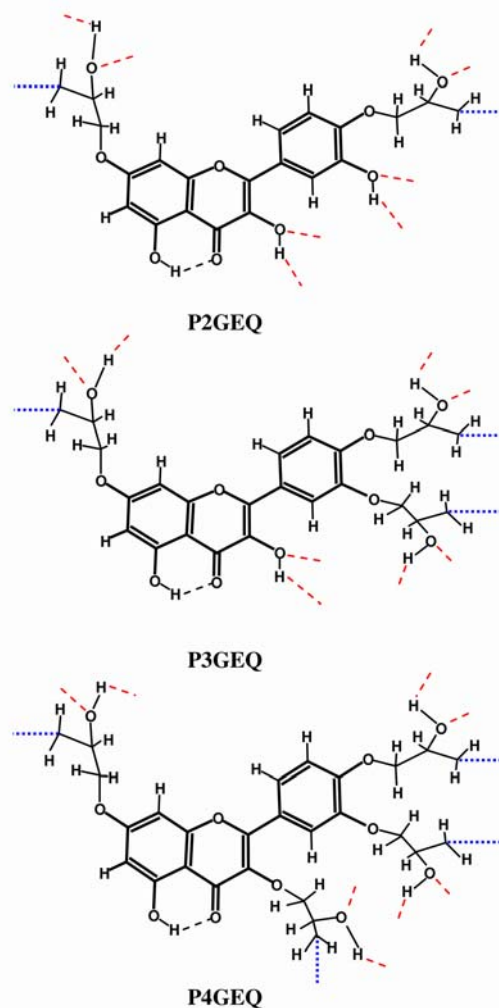


Fig. 1. Structures of polymer network segments of P2GEQ, P3GEQ, P4GEQ. Dashed lines — hydrogen bonds participating in physical bond formation, dotted lines — chain covalent bonds with other network segments.

$$\text{GelContent}[\%] = (M_0 / M_1) \cdot 100, \quad (2)$$

where  $M_0$  is initial weight of the specimens before extraction;  $M_1$  is final weight of the specimens after extraction.

Each quantitative determination of the residual solvent concentration, as well as  $M_c$  and  $\nu_c$  values were made in five replications.

UV-visible spectra of the polymer films by UV-VIS Spectrophotometer Hitachi-U3210 in the range of 210–500 nm were recorded. Mathematical treatment of the spectra was performed using Spectra Data Lab software package [13]. The thickness of the films was measured by interferometer of the Lyytik type.

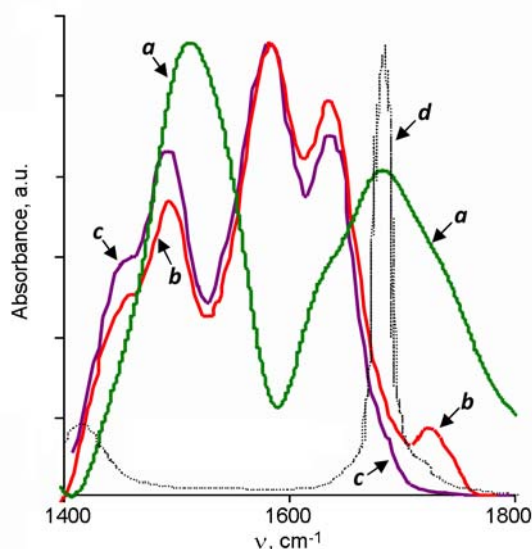


Fig. 2. FTIR-ATR spectra of film based on P4GEQ in the range of 1400–1800  $\text{cm}^{-1}$  after drying at the room temperature (a), unannealed after poling (b) and annealed (c).

Three series of the polymer films were prepared. The polymer films of the first series were dried under the room temperature during 24 h with weight control by the microgravimetric method. The polymer films of the second and third series were not only dried as in the first series, but also poled (2nd series) and annealed till the weight stayed constant at 80°C for 3 h (3rd series).

### 3. Results and discussion

#### 3.1. Influence of residual solvent on polymers structural parameters

Figure 2 shows FTIR-ATR spectra of the P4GEQ polymer films: after drying at the room temperature (a), unannealed after poling (b), annealed (c) and pure solvent (acetone) (d). Similar spectra were also obtained for P2GEQ and P3GEQ polymer films.

In the spectra of the films dried at the room temperature there is a wide intense band with maximum at 1710  $\text{cm}^{-1}$  corresponding to this of pure acetone and due to C=O groups stretching. The mentioned band contains also two shoulders at 1655  $\text{cm}^{-1}$  and 1740–1750  $\text{cm}^{-1}$ . The first one is due to stretching of pyrone carbonyl groups of the quercetin fragments, the second one can be explained by C=O groups stretching of acetone molecules hydrogen-bonded with polymer chains. The spectra of after-poling films demonstrate maxima at 1655 and 1745  $\text{cm}^{-1}$ ; the band at 1710  $\text{cm}^{-1}$  is ab-

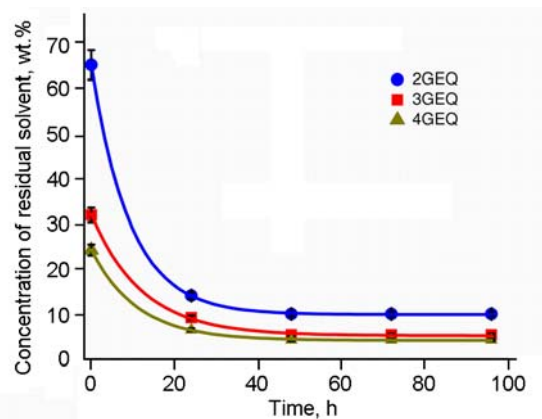


Fig. 3. Kinetics of removal the residual solvent (acetone) from polymer films.

sent. Thus, one can conclude that the poling process results in complete removal of free solvent, but not of hydrogen-bonded acetone molecules.

In the FTIR spectra of the annealed polymer films, absorption bands of acetone carbonyl groups were not detected. It evidences that the annealed polymer films do not contain the residual solvent in detectable concentrations.

As it was mentioned above, changing of the solvent content in the polymer films under drying was investigated using the microgravimetric method. Since the amount of the solvent removed depends on many factors, particularly, such as the mutual diffusion coefficient of the solvent-polymer system, the film thickness and drying time, the estimations of solvent content were therefore carried out in the films of equal thickness — 1  $\mu\text{m}$ , at the same temperature, and under similar duration of the experiment.

Variation of the residual solvent concentration in the studied polymer films with time is shown in Fig. 3. All the dependences presented demonstrate two characteristic areas.

The first area corresponds to drying period, which occurs for all the polymers in time interval from the beginning of experiments to 24 h, approximately. During this period, the dependence of the residual solvent concentration on time demonstrates exponential decay in accordance to the first Fick's law [14]. The rate of the solvent transport to/through the surface followed by its solvent removal from the polymers decreases. It is due to decrease of the solvent content in the polymer films and to formation of a solvent-deficient layer near their surfaces.

Table. Structural parameters of cross-linked polymer films before and after annealing

Materials	* $v_c$ , mol·m <sup>-3</sup>	* $M_c$ , kg·mol <sup>-1</sup>	** $v^{solv}_c$ , mol·m <sup>-3</sup>	** $M^{solv}_c$ , kg·mol <sup>-1</sup>	$\omega$ , %
P2GEQ	7595	0.210	3078	0.518	59
P3GEQ	4997	0.308	3086	0.499	38
P4GEQ	4196	0.367	3409	0.452	20

\* $v_c$ ,  $M_c$  are effective cross-linked densities and molecular weights between cross-linking units of annealed polymeric films; \*\* $v^{solv}_c$ ,  $M^{solv}_c$  are effective cross-linked densities and molecular weights between cross-linking units of unannealed polymeric films;  $\omega$  is the degree of  $M_c$  decrease after solvent removal.

The second period corresponds to time interval from 24 h to the experiment end moment. During this period the residual solvent concentrations were not changed and were equal to 4 wt.%, 6 wt.% and 10 % wt. for 4GEQ, 3GEQ and 2GEQ polymer films, respectively. The incomplete removal of the residual solvent can be explained as by non-covalent interactions (hydrogen-bonded complexes) between carbonyl group of acetone molecules and hydroxyl groups in the polymer 3D networks, as by non-specific interaction between solvent molecules.

Breaking the hydrogen bonds and complete removal of the solvent can be achieved when drying under the high temperatures [15]. It worth to note that heating of the specimens under conditions corresponding to the poling process ( $t = 200^\circ\text{C}$  during 1 h) is not sufficient to remove all the residual solvent from the polymers. The concentrations of this last in the films were about 0.1–0.5 %. Stated above, the residual solvent was not observed in all polymer films annealed during 3 h at  $t = 100^\circ\text{C}$ . Comparing the conditions of the polymer poling and annealing, one can conclude that time factor is more decisive than temperature of the specimens. It is obvious that the complete removal of the solvent is not so much determined by the hydrogen bonds breaking as by time necessary for solvent diffusion in the polymer phase with followed solvent evaporation from the film surface.

An important factor influencing on the solvent removal under drying and annealing processes is the existence of "holes" — discontinuities in molecular packing, which conditions the presence of free volume in the polymer phase [16]. According to the "free volume" theory, polymer contains dynamic "holes" of various sizes. If a "hole" volume is equal or larger than that of a solvent molecule, then this last can migrate through this "hole" to another polymer cav-

ity. Thus, the "holes" sizes control the diffusion process.

In the case of cross-linked polymers, an average "hole" size has to depend on the chain length between the cross-linkes units, which can be characterized by such quantitative structural parameters as effective cross-linked density ( $v_c$ ) and molecular weight between the cross-linked units ( $M_c$ ) [11]. The higher average "hole" size corresponds to the lower  $v_c$  and to the greater  $M_c$ . The  $v_c$  and  $M_c$  parameters for studied polymer films are listed in Table.

The "hole" sizes could hardly change during the drying process at approximately constant temperature of the medium. In the cases of the high-temperature processes such as poling or annealing, it would be reasonable to expect an increase in the size of the "holes" due to thermal motion of the chain segments, and its decrease to former size after cooling. However, the data in Table show that removal of the solvent under the annealing results in substantial decrease of the "hole" size. The minimal  $M_c$  fall is observed in the case of P4GEQ polymer having the highest branching degree, and, on the contrary,  $M_c$  value decreases up to 59 % in P2GEQ polymer with the minimal branching. The  $M_c$  changing linearly correlates with residual concentration of acetone before annealing ( $r = 0.989$ ) that suggests a substantial influence of the solvent on the polymer network structures.

The observed phenomenon can be explained if one supposes that formation of the hydrogen bonds between the solvent molecules and polymer chains prevents finishing the polymer network formation. The solvent molecules, which fill the space inside the "holes", can hinder contacts of functional groups of neighboring polymer chains and thereby prevent formation of crosslinks (Fig. 4a). The presence of hydrogen bonds between solvent molecules, as well as between the functional groups and the solvent molecules, renders this system

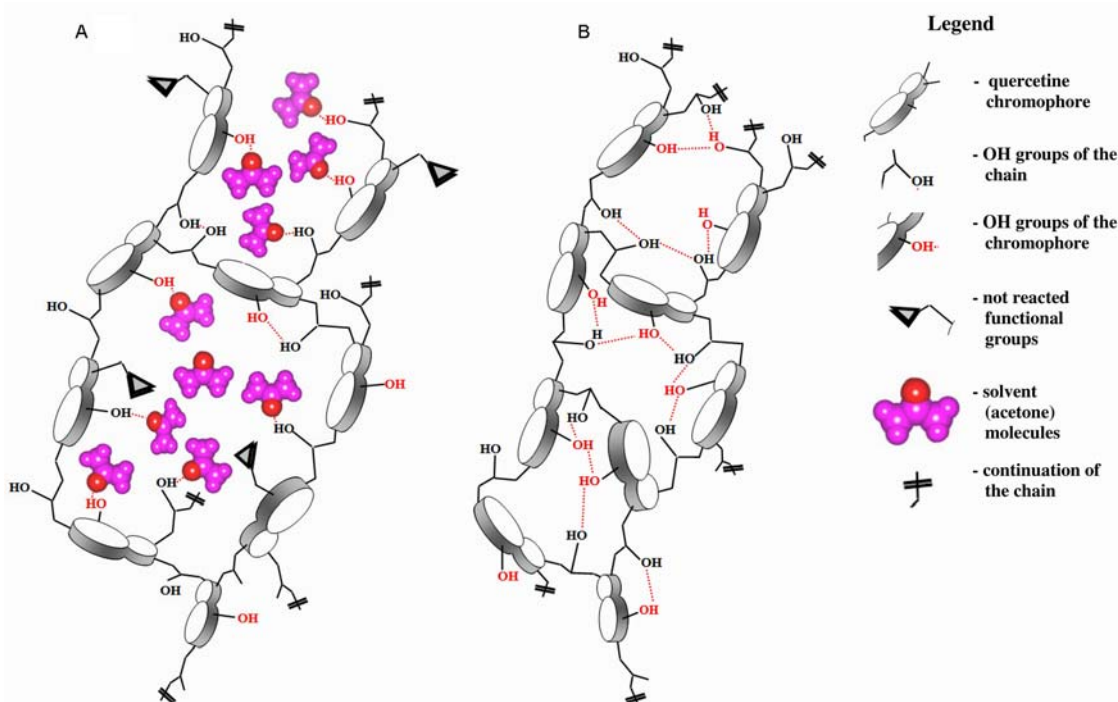


Fig. 4. Hypothetic structure of polymer chain before (A) and after annealing (B).

more rigid that additionally decreases the possibility of the cross-linking. Because of the incompleteness of the polycondensation process, the polymer network contains "free ends" — not reacted functional groups existing in the form of spacers attached to the carcass of the polymer network.

When finishing annealing process, i.e. after solvent removal followed by cooling polymer, the "holes" shrink to their natural "solvent free" size that results in contacts of the free functional groups followed by their interaction and formation of the new crosslinks. In the case of P4GEQ having higher branching and, correspondingly, greater carcass rigidity, the solvent removal leads to the lesser changes of the "hole" size and, consequently, to the lesser additional cross-linking. And vice versa, the P2GEQ polymer with the lower degree of branching has minimal carcass rigidity. In the result, this polymer has maximal  $M_c^{solv}$  value and, correspondingly, the greater "holes" size in the presence of the residual solvent. After removal of the latter, the greater approachment of polymer chains takes place that leads to additional cross-linking and to the decrease of  $M_c$  value (Fig. 4b).

### 3.2 Influence of residual solvent on relaxation behavior of polymer films

The second-order NLO properties of polymer films are results of ordered orientation of chromophore fragments, attached to the polymer chains or being segments of these last. After the poling process resulting in the chromophore ordering and in appearance of anisotropy of optical properties, the opposite process of relaxation, which disorders the chromophores due to the thermal motion of fragments of the polymer molecules, takes place. Investigations of the relaxation influence on the second-order NLO properties of the polymer films are usually carried out by monitoring the decay of the order parameter ( $\Phi$ ) as a function of time at 25°C. The order parameter can be calculated according to equation [17]:

$$\Phi = 1 - A_1/A_0, \quad (3)$$

where  $A_0$  and  $A_1$  are absorbances of polymer films before and after corona poling, respectively.

Recent investigations of annealed and, then, poled polymers of P2GEQ, P3GEQ and P4GEQ [18] showed that relaxation processes depend on two important conditions—cross-linking degree, which determines the "holes" sizes, and the presence of hydrogen bonds between hydroxy groups of quercetine chro-

mophore fragment and other proton-donating and proton-withdrawing fragments of the polymer chains. Thus, P4GEQ polymer with minimal cross-linking degree (see corresponding  $v_c$  and  $M_c$ ), whose quercetin chromophore fragments do not form hydrogen bonds with polymer network, has fast relaxation dynamics. The value  $\Phi$  of this polymer decreases almost two times during one month.

Annealed P2GEQ and P3GEQ polymers have higher cross-linking degree, 3-hydroxy groups of their chromophore fragments form the hydrogen bonds with the polymer network. That is why, these polymers demonstrate substantially slower relaxation dynamics: their NLO properties retain during a long time. The greater stability of the NLO properties is typical for P3GEQ polymer.

The results of relaxation dynamics investigations for the polymers containing the residual solvents are depicted in Fig. 5. It can be seen that the dynamics of the relaxation processes in solvent-containing polymers can drastically differ.

Figure 5c shows that plots of the  $\Phi$  values against the relaxation time are similar for the annealed and solvent-containing P4GEQ polymer. Such a relaxation behavior of the polymers seems to be logical: their chromophore fragments have no hydrogen bonds with the solvent molecules and the polymer network, and, according to the values of  $v_c$  and  $M_c$ , their "holes" are of close sizes.

In the case of annealed and unannealed P2GEQ and P3GEQ polymers, a drastic difference in relaxation dynamics was observed. Since the "hole" sizes in these polymers are approximately similar ( $M_c^{solv}(P2GEQ) \approx M_c^{solv}(P3GEQ)$ ), the difference in relaxation behavior could be due to different character of hydrogen bonding between the quercetin chromophore and the polymer network.

We suggest the following explanation of the observed phenomena. In the solvent-containing polymers, 3-hydroxy groups of some quercetin fragments form hydrogen bonds not only with the polymer network that fixes the chromophore positions, but also with the movable solvent molecules that, on the contrary, leads to increase of the chromophore mobility and simplifying the relaxation processes (Fig. 4a).

Thus, unlike annealed P3GEQ, whose samples keep NLO properties during a long time, solvent-containing P3GEQ undergoes the relaxation process. According to Fig. 5b, approximately 5 % of chromophore

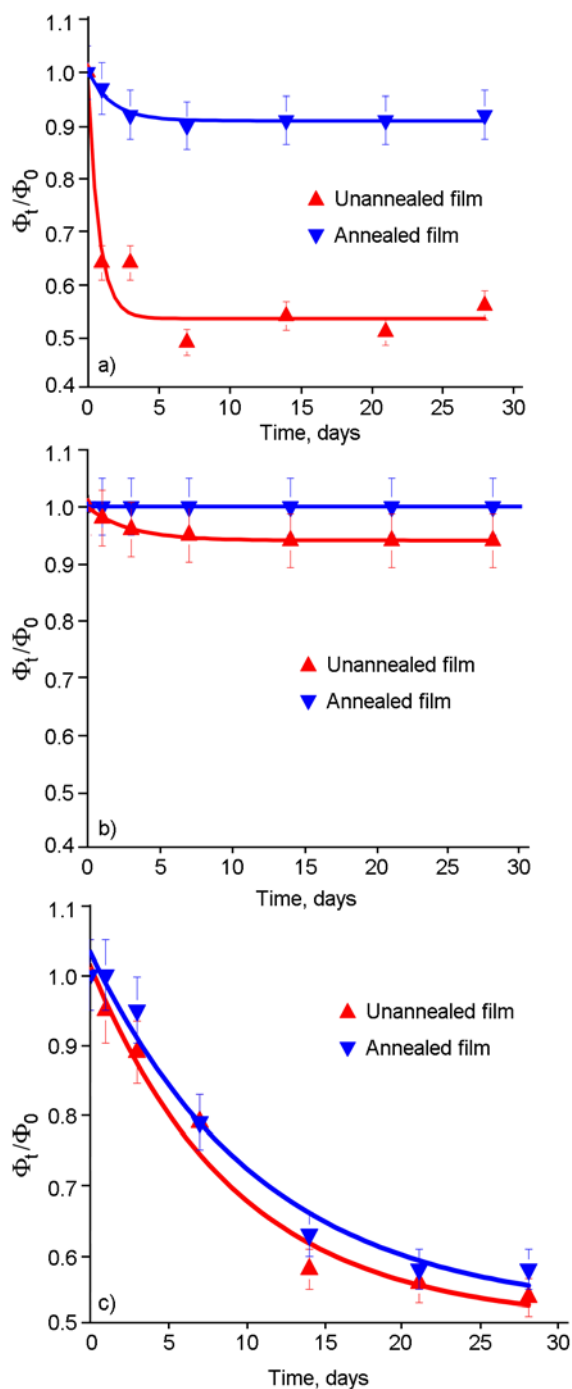


Fig. 5. Time decay of the  $\Phi_t/\Phi_0$  value of the poled annealed and unannealed polymer films at ambient temperature based on: a) P2GEQ; b) P2GEQ; c) P4GEQ.

fragments change their initial orientation during 5–7 h.

Quercetine chromophores of P2GEQ have two hydroxy groups in positions 3 and 3' and can correspondingly form two hydrogen bonds. In our previous article [18] it was shown in that presence of second 3'-hydroxy group resulted in a little destabilizing ef-

fect: annealed P2GEQ demonstrated greater relaxation ability due to additional regrouping of physical network accompanying by partial de-ordering of the chromophores. The relaxation time was found to be 5 h approximately, the  $\Phi$  value decreased until 10 %.

In the presence of residual solvent, two hydroxy groups of P2GEQ chromophore fragments form the substantially greater quantity of hydrogen bonds with the solvent molecules that increases flexibility of the polymer chain segments and leads to the greater relaxation ability. The relaxation time of solvent-containing P2GEQ was similar to that of P3GEQ, however the decrease of the  $\Phi$  value achieved 45 % (Fig. 5a).

#### 4. Conclusions

The investigations of cross-linked polymers based on glycidyl derivatives of 3, 5, 7, 3', 4'-pentahydroxyflavone showed that presence of residual solvent influences substantially on structure of the polymer network, and, consequently, on physico-chemical properties of corresponding polymeric materials. The residual solvents cannot be removed by drying at ambient temperature and at short-time heating when poling the polymer. A complete removal of the solvent can be achieved only by annealing the polymers during 3 h at temperature of about 100°C. The drying at these conditions is accompanied by additional cross-linking of the polymer chains.

The comparison of physico-chemical properties of the polymers obtained on the basis of di-,tri- and tetraglycidyl quercetin before and after annealing were carried out by studies of changing their NLO properties, namely of the relaxation dynamics — de-ordering the chromophore fragments after poling. It was shown, that the pres-

ence of the residual solvent leads to increase of the relaxation processes in the polymers and, hence, to significant weakening of their NLO activity over time.

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