Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Polyamide-12/Polyaniline Layered Composite Films: Specificity of the Formation and Raman Spectroscopy Investigation

A. A. Pud[a]; K. Yu. Fatyeyeva[ab]; J. -F. Bardeau[b]; S. P. Rogalsky[a]; M. Tabellout[b]; G. S. Shapoval[a]
[a] Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, Kyiv, Ukraine [b] Laboratoire de Physique de l'Etat Condensé, Université du Maine, Cedex, France

To cite this Article Pud, A. A. , Fatyeyeva, K. Yu. , Bardeau, J. -F. , Rogalsky, S. P. , Tabellout, M. and Shapoval, G. S.(2007) 'Polyamide-12/Polyaniline Layered Composite Films: Specificity of the Formation and Raman Spectroscopy Investigation', Journal of Macromolecular Science, Part A, 44: 2, 183 — 192

To link to this Article: DOI: 10.1080/10601320601031358

URL: http://dx.doi.org/10.1080/10601320601031358

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2007) **44**, 183–192

ISSN: 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320601031358

Polyamide-12/Polyaniline Layered Composite Films: Specificity of the Formation and Raman Spectroscopy Investigation

A. A. PUD,[1] K. Yu. FATYEYEVA,[1,2] J.-F. BARDEAU,[2] S. P. ROGALSKY,[1] M. TABELLOUT,[2] and G. S. SHAPOVAL[1]

[1]*Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, Kyiv, Ukraine*
[2]*Laboratoire de Physique de l'Etat Condensé, Université du Maine, Cedex, France*

Received May, 2006, Accepted June, 2006

Composite polyamide-12/polyaniline (PA-12/PANI) films were prepared by a treatment of PA-12 films swelled in aniline with a water solution of ammonium persulfate (APS) and HCl. The existence of a very thin (2 μm) subsurface PANI containing layer in the composite film was shown by confocal micro-Raman resonance spectrometry. A combination of the micro-Raman and UV–Vis measurements allowed determining the PANI concentration in this conductive layer. This approach allowed studying the kinetics of the matrix polymerization process. It is shown that this solid phase process has the strong kinetic specificity as compared with known solution based systems. It is suggested that this is due to not only the physical-chemical interactions of aniline and formed PANI with amide groups of the matrix but also to a physical state of aniline localized in voids of the free volume of the matrix and to formation of the additional oxidant HOCl in the oxidizing solution.

Keywords: aniline; matrix polymerization; polyamide-12 film; kinetics; UV-Vis and Raman spectroscopy; interaction

1 Introduction

Composite materials of intrinsically conducting polymers (ICP) and common polymers attract much attention due to their wide range of applications, such as antistatic materials, electromagnetic interference (EMI) shielding, sensor and membrane materials (1–3). Because of the infusibility, insolubility and poor mechanical properties of ICP, such composites are also an effective way of processing intractable ICP (2, 4, 5). As compared to traditional carbon and metal filled conducting composites, the main advantages of the composites based on ICP are their better mechanical properties due to a much less content of conducting phase, low percolation threshold, an additional unique complex of sensor, electrophysical, optical, membrane and other properties (2, 3). Among ICP composites, PANI ones are considered as being the most environmentally stable and inexpensive (1–3). Properties of such materials are easily modified by changing the PANI doping level (6), dopant nature (3, 7) and the monomer structure (8, 9).

On the other hand, it is clear that a nature of a polymer binder (matrix) has a significant influence on the PANI composite properties. Specifically this factor is very important when the aniline polymerization is performed inside a polymer film to form the PANI composite (2, 3, 9–13). For example, it was previously reported (11) that the polymerization of aniline in a semi-crystalline poly(ethylene terephthalate) (PET) film by the traditional technique–treatment of the aniline-containing film in an acidified water solution of APS was unsuccessful. However, it was realized in a chlorine water solution under an oxidative action of HOCl. In this case, the process penetrated into the matrix and resulted in formation of PANI inside of ~1 μm layer beneath the matrix surface (11).

Unlike the PET/PANI composite layered film (11), conducting transparent Nylon-6/PANI composite layered films can be easily prepared by immersing the aniline-containing polyamide (Nylon-6) film in a APS water solution (10). Byun and Im (10) assumed that the process run in an outer layer of the composite film. This layer retarded diffusion of the oxidant solution into the matrix and hindered the formation of PANI inside the film, correspondingly (13).

In all probability, the difference in the selectivity of the PET/aniline (11) and Nylon-6/aniline (10) films to the oxidants may be explained in terms of their wettability and ability to absorb water solution with all its components. This difference can be enhanced by kinetic limitations in

---

Address correspondence to: A. A. Pud, Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, 50 Kharkivske Shose, 02160, Kyiv, Ukraine. Tel/Fax: +38 044 5597063; E-mail: echoc@mail.kar.net, echoc@mail.vtv.kiev.ua

penetration of nondissociated (HOCl) or dissociated charged (HCl, APS) forms of the solution components into the dielectric solid matrix. Moreover, in this connection hydrogen bonding between aniline/PANI and the matrix, as well as structure of the matrix (3, 10, 11), can also be considered as important factors.

It is also obvious that all the above-mentioned factors should affect aniline polymerization kinetics, thickness and properties of the PANI containing layer formed in the matrix. Revealing these factors and their relationships could be useful for better understanding the process of formation of the dielectric polymer/PANI composites. Toward this end, and due to thin thickness and optical transparence of the PANI containing layer in this kind of the composite materials, UV-Vis spectroscopy can be applied to study the PANI formation process and its properties (11). Vibrational spectrometry is also very suitable here due to its extreme sensitivity to the electronic structure changes in PANI (14). Specifically, Resonance Raman spectrometry allows distinguishing different states of PANI involving both oxidation and protonation (15, 16), which can be different in PANI-containing composites depending on the preparation conditions and a dielectric polymer structure.

Using these spectral techniques, our aim with this paper is to make clearer a specificity of aniline polymerization in a solid phase semi-crystalline polymer matrix. As the convenient matrix object, the polyamide PA-12 film was chosen because it was intermediate between PET and Nylon-6 matrixes hydrophilicity. This allowed running the aniline polymerization inside the PA-12 in APS acidified water solution, unlike the above-mentioned PET case (11). On the other hand, the polymerization in PA-12 ran at a much lower rate than inside the Nylon-6 matrix that allowed easy registration of the PANI formation by UV-Vis spectroscopy and to find kinetic parameters of the process.

2 Experimental

2.1 Materials

Aniline (Merck) was distilled under vacuum and stored under argon in a refrigerator at 3°C. *N*-methylpyrrolidone (NMP) (Aldrich), APS (Ukraine), n-hexane (Ukraine) and hydrochloric acid (Ukraine) were of reagent grade and used as received. Films of PA-12 of 50 μm thickness and degree of crystallinity at 20.8% were kindly donated by Arkema (France).

2.2 Preparation of the PA-12/PANI Layered Composites

Prior to use, samples of PA-12 films were washed with n-hexane. This was followed by their swelling in a vessel containing aniline at 20 ± 1°C for different periods of time. The films impregnated with aniline were washed by n-hexane to remove a surplus of monomer from their surface, then weighed and used in the kinetic polymerization experiments or to prepare PA-12/PANI layered composites for further investigations. These experiments were realized at different molar concentrations, both of aniline in the films and of the oxidant (APS) in the reaction solutions. For simplicity, the aniline molar concentrations in the films were calculated on the basis of a rough assumption of homogeneous distribution of aniline in the whole film, similar to the calculations for real solutions.

In general, the kinetic polymerization procedure was practiced as follows. The strip (10 mm × 30 mm) of the aniline-containing film was placed into the quartz cuvette (path length: 10 mm) filled with 3 ml of the APS solution in 1 M water hydrochloric acid. This allowed direct kinetic control of the PANI formation process in surface layers at both sides of the transparent matrix by UV-Vis spectroscopy. The time of placing the film in the oxidant solution was noted as the starting point of the polymerization. The UV-Vis measurements were carried out in the spectral range of 300-900 nm with the help of a spectrometer Specord M-40 (DDR).

For the Raman spectrometry measurements, the PA-12/PANI layered composites were prepared in an another manner, namely by fixation of the PA-12 film (50 mm × 75 mm) with aniline in a special home-built cell allowing contact of only one side of the film with the oxidant solution. The final samples were of a double-layered structure – the first thin surface layer consisted of PANI distributed in the PA-12 matrix and the second was pure PA-12.

After completion of the process, the green transparent films were taken from the oxidant solution, then washed with distilled water and placed in Soxhlet's apparatus for 5 h to extract n-hexane aniline livings and by-products. This procedure was followed by drying the films under dynamic vacuum up to a stable weight.

Surface conductivity of the prepared samples was measured at room temperature by a standard two-point probe technique. All the samples showed conductivity in the range of $10^{-5} - 10^{-6}$ S/sq.

In order to convert the PANI formed in the emeraldine salt (ES) state inside the polyamide matrix to the nonconducting emeraldine base (EB) state, the composite film was treated with a water solution of 5% NH_4OH for 24 h.

2.3 Resonance Raman Spectrometry Measurements

Confocal micro-Raman resonance spectrometry was used to check the presence and oxidation state of PANI inside the subsurface layer of the composite polyamide films. The vibrational investigations of the composite films as a function of the depth allowed the estimation of the thickness of the PANI containing layer.

The experiments were carried out by a multi-channel Jobin-Yvon T64000 spectrometer connected to a liquid N_2 cooled CCD detector. The resonance Raman scattering studies were performed with $\lambda = 514.5$ nm laser excitation (green excitation line). This line was chosen to provide enhancement of the Raman bands of phenyl and quinone units of PANI (15, 16). In order to investigate the vibrational properties of different polymer forms of PANI, the Raman measurements were focused mainly within the 1100-1700 cm^{-1} region. In order to avoid any local degradation of the composite films, the laser beam power was intentionally limited to 0.04 mW on a sample surface and the spectra were collected with an integration time of 300 s. The laser beam was focused on the sample in a cca 1 μm spot size by a ×100 objective and the spectral resolution was approximately 1.5 μm.

Initially, we measured the virgin PA-12 film, the pure doped PANI powder and the composite film (Figure 1). The enhancement of the bands of PANI is clearly observed while the bands of PA-12 are very weak when it is recorded under the same experimental conditions. For this reason, the spectrum is not characterized by any well-defined band of PA-12 (Figure 1, curve 1). On the contrary, the features observed on the Resonance Raman spectrum for the PA-12/PANI film (Figure 1, curve 3) are similar to the vibrational bands for the pure doped PANI powder (Figure 1, curve 2). The bands assignment is presented below in the *Raman Spectrometry* section.

On the basis of the obtained results, and taking into account the advantage of the confocal system, we may conclude that no contribution of the PA-12 vibrational bands should be taken when we will analyze the intensity evolution of the PANI bands as a function of depth. Raman spectra were recorded through the thickness of the composite film using a PI motor stage allowing displacement of the sample below the objective (Figure 2a). The bands of the obtained spectra (Figure 2b) were compared with bands of the pure doped PANI powder (Figure 1, curve 2) and the dependence of the integrated Raman intensity of PANI vibrational bands in the 1100-1700 cm^{-1} range was plotted vs. a sample position (Figure 2c).

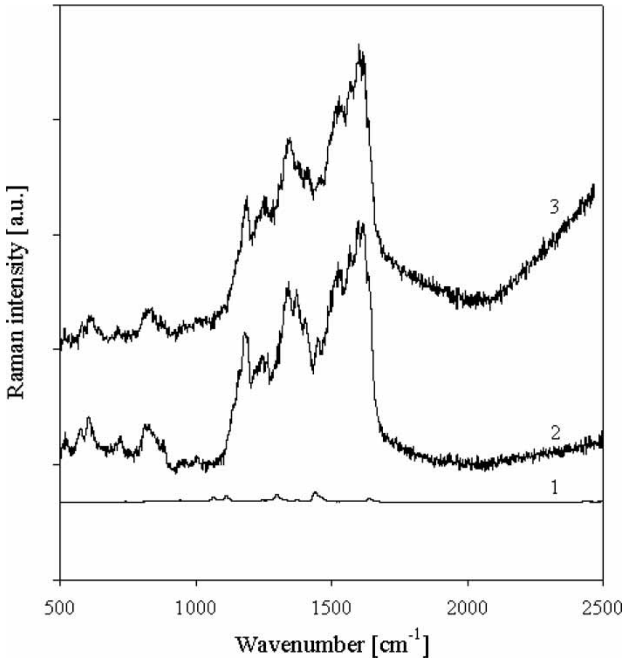

Fig. 1. Raman spectra collected under the same experimental conditions ($\lambda = 514.5$ nm, t = 300 s, p = 0.04 mW) of the PA-12 film (*1*), PANI in the form of ES (*2*), the composite PA-12/PANI doped film (*3*).

The depth analysis of the composite showed that the thickness of the PANI containing layer was 2 μm. This value was determined by taking into account the refractive index of PA-12 and the full-width at half-maximum of the Raman profile (1.3 μm 1.54 = 2 μm). This value was used in the further calculations of the PANI yield in the composite films.

2.4 *Evaluation of the PANI Yield in the Composites*

This point was very important for a treatment of the kinetic results. Therefore, some efforts were directed to evaluate a real quantity of PANI formed inside the surface/subsurface layer of the PA-12 matrix. In order to do this, we previously synthesized EB form of PANI according to (17). UV-Vis spectra of EB solutions in NMP were obtained that allowed us to get a dependence of the solution optical density on EB concentration at $\lambda = 647$ nm (absorption of quinonediimine groups). This calibration curve was further used to determine a quantity of EB in the surface/subsurface layer of the composite films.

Specifically, this determination procedure was based on two points: 1) a similarity of UV-Vis spectra of PANI in EB form both in the solid PA-12 matrix and in liquid NMP; and 2) postulate the equality of extinction coefficients of EB in the both amide media. Correspondingly, it was accepted that a quantity and concentration of PANI base in the surface layer of the composite film might be calculated from a calibration curve of EB concentration in its NMP solution. The thickness of this layer (2 μm) was found from the Raman depth analysis of the composite (see the section on *Resonance Raman Spectrometry Measurements*).

3 Results and Discussion

3.1 *On Specificity of Aniline Matrix Polymerization*

Let us consider briefly some specific features of aniline polymerization in a solid polymer matrix. The polymerization process begins at the interface between the matrix, which contains aniline, and an acidified oxidant water solution. Obviously, the condition of the matrix surface dictates a specific orientation of presenting aniline molecules that, in turn, strongly affects features of this process. A similar effect of the molecular orientation was suggested by Bodalia et al. (18) in the case of 2-pentadecylaniline polymerization in monolayer at the air-water interface (Langmuir-Blodgett technique), for example.

Unlike a typical aniline (more precisely, anilinium cation) polymerization in a solution, this process in the

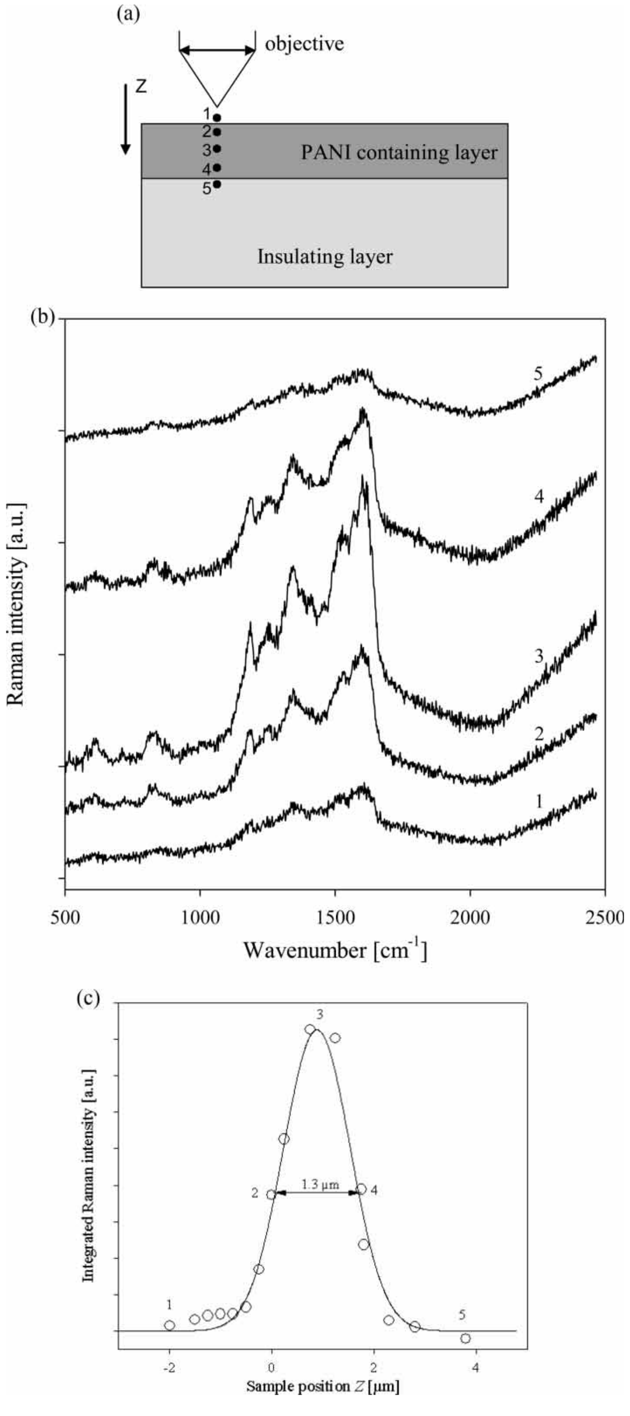

Fig. 2. (a) Schematic presentation of the Raman depth analysis; (b) Raman spectra of the composite PA-12/PANI doped film at different sample position ($\lambda = 514.5$ nm, t = 300 s, p = 0.04 mW); (c) Integrated Raman intensity of PANI vibrational bands in the wavenumber region 1100-1700 cm^{-1} for the composite PA-12/PANI film.

aniline-containing matrix, after its contact with the oxidizing solution, should involve a previous aniline protonation step before an oxidation stage. However, to participate in these stages, both the acid and oxidant should diffuse from the solution bulk to the matrix surface. The aniline polymerization begins as the two-dimensional process with some fixed rate. Naturally, a further development of the polymerization process into the matrix bulk (three-dimensional level) has a much lower rate because it is strongly limited by a slow penetration (diffusion) of the reagents into the matrix polymer. A few more points seem to be important for the matrix polymerization process and properties of PANI, which is forming in the matrix. Specifically, an orientation of aniline molecules in the matrix depends on their physical-chemical interaction with polar groups of the matrix polymer (3, 12). Furthermore, in a semi-crystalline polymer matrix (e.g. PA-12), the monomer should preferably be localized in a free volume of an amorphous part distributed among crystalline regions. This suggests that in some spaces (voids) of the free volume aniline can be located as a separate nano/submicron sized undiluted liquid phases. Correspondingly, the aniline matrix polymerization should have some kinetic specificity as compared with the solution polymerization case. Specifically, an increase of the induction period (IP) of the aniline matrix polymerization as compared to the similar process in a solution (19) may be an important consequence of the above features. The other specificity stems from the solid phase nature of the matrix and leads to an immobility of aniline dimers and other oligomers, which are actually fixed (trapped) in the free volume of the matrix due to their large size and different intermolecular interactions. This results in the fact that the chain propagation step can be realized only through diffusion of the monomer to these trapped oligomers. This limitation is much stronger than in the case of 2-pentadecylaniline polymerization in the liquid monolayer (18). Moreover, one may not exclude the fact that the oxidation reaction of aniline (more precisely, anilinium cation) in the matrix bulk can be transmitted to some extent from the interface due to oxidation of oligoaniline chains, which act, in this case, similarly to conducting nano/microelectrodes and intergrow into the matrix due to interaction with the monomer molecules located there. Partly, this possibility is a consequence of hindered diffusion of a large inorganic oxidant (e.g. APS) into the matrix. The other important practical issue of the matrix polymerization process is that, unlike the aniline solution polymerization (19, 20), there is no problem with the PANI precipitation. All the forming aniline oligomers and PANI actually remain in the solid solution or dispersion i.e., the matrix plays a role of solid phase solvent. This allows easy observation of the process peculiarities, which run inside transparent polymer films.

Finally, all the considered factors, which determine the matrix polymerization specificity, allow the presumption that they should also affect the distribution of the conducting PANI network and properties of the ultimate composite.

3.2 Kinetic Peculiarities of the PANI Formation in PA-12 Film

Visually, aniline polymerization in the PA-12 film placed in the acidified APS solution runs through formation of separated blue regions at the film surface. These regions rapidly change their color to green and merge gradually in the course of polymerization that imparts green color to the entire film surface. These color changes testify that the PANI formation in the matrix is realized through typical stages of pernigraniline and ES formation. However, the UV-Vis spectra obtained during the aniline polymerization process did not display the stage of pernigraniline formation probably because of the large time gap (~3–10 min) between the spectra. But the formation of PANI in ES state in the film is clearly revealed (Figure 3). In the spectra a typical set of bands of forming ES is observed: the first one at 340 nm is assigned commonly to π-π^* transition of benzene rings, the shoulder at cca 440 nm and a broad band at cca 750 nm are obviously polaron transitions (19, 21). Intensity of these bands increased during the reaction (Figure 3).

It should be noted that these features of the spectra strongly differ from those obtained by Neoh et al. (22) in the case of aniline polymerization inside Nylon-6 matrix, which is similar by nature to PA-12. Specifically, after 10 min polymerization they registered an appearance in the UV-Vis spectrum of strong bands at 280 and 620 nm and a weak one at 320 nm assigned to protonated pernigraniline. This spectrum was easily changed by simple quenching with deionized water for 30 min to the spectrum of pernigraniline base, which contained bands at 280, 320 and 520 nm. However, the more interesting phenomenon was the transformation of these bands after reprotonation with HCl to bands of ES (340, 420 and 750 nm) (22) that obviously testified to a reduction of PANI in the pernigraniline state to the emeraldine one during the used protonation procedure. Comparing the UV-Vis spectra presented in Figure 3, and the results reported by Neoh et al (22), one can say that the aniline polymerization in the PA-12 matrix runs much slower than in Nylon-6, even at a high concentration of aniline. This difference may be related both to a much higher rate of penetration of the oxidant solution into the more hydrophilic matrix of Nylon-6 and to the oxidant concentration (0.25 M (22)) increased as compared with our procedure (0.1 M). These two factors were probably responsible for a fast diminishing of the PANI bands, followed by their disappearing due to an overoxidation process when prolonging the polymerization time in the Nylon-6 film for more than 10 min (22). To make a pertinent comparison of the aniline polymerization as a function of the matrix nature, we realized this process in the Nylon-6 film under the same conditions used in the PA-12 case. It was observed by *in situ* UV-Vis spectroscopy that the polymerization process in the Nylon-6 film resulted in the formation of ES rather than protonated pernigraniline, unlike Neoh et al. data (22). But this process ran much faster than in the PA-12 film and, was accompanied by a rapid degradation of formed PAN, followed by decoloration of the composite film as was observed by Neoh et al. (22).

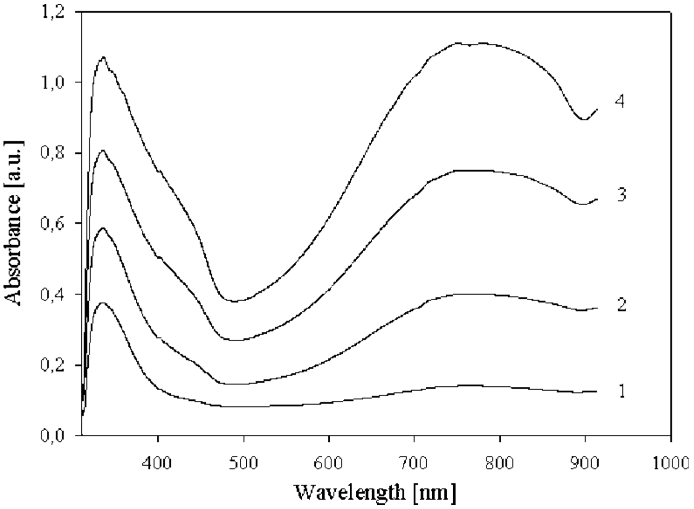

Fig. 3. *In situ* absorption spectra of the PANI formation in the PA-12 film (solution 1 M HCl + 0.1 M $(NH_4)_2S_2O_8$, $C_{aniline} = 1.36$ M) at different time: *1*–7.2 min; *2*–17.6 min; *3*–22.6 min; *4*–30.9 min.

In the case of the PA-12 film, the bands of forming PANI grew during the polymerization for a long time (up to 6 h) followed by some deceleration of this process. That was accompanied by a very slow widening of the broad band at cca 750 nm to the blue side of the spectrum (Figure 3). Such behavior probably displayed a deeper oxidation and/or overoxidation of PANI formed inside upper layers of the PA-12 matrix, which constantly contacted with the oxidant solution.

As it follows from the known kinetic studies of aniline polymerization (19–21, 23, 24), on the assumption of other conditions being equal, the factors which control kinetics of this process are aniline and oxidant concentrations. That is, at first sight, the main reason of the process rate deceleration could be a depletion of aniline in the matrix. However, in accordance with our Raman measurements, PANI was formed in thin surface layers (thickness 2 μm, see Experimental) at both sides of the PA-12 film. That means that the aniline polymerization occurred in these two layers being in fact the reaction zones of the same thickness. As a consequence, localized between these layers the internal part of the aniline-containing film (46 μm left) may be considered as an inexhaustible source of aniline, which diffuses into the reaction zones. Therefore, the depletion of aniline in the matrix seems to be the unlikely reason of the polymerization rate deceleration.

On the other hand, penetration into the reaction zone of the inorganic oxidant and the acid, which are necessary to initiate the chain propagation, is strongly limited by a small ability of the hydrophobic PA-12 matrix to swell in water mediums. Specifically, we have found that this matrix is able to swell for 7 h in distilled water, in 1M HCl and in 0.1M $(NH_4)_2S_2O_8$ acidic (1M HCl) water solutions only up to 1.07 wt%, 1.77 wt% and 2.32 wt%, respectively (Figure 4). Obviously, this factor determined the small thickness (2 μm) of the reaction zone. As a consequence, we obtained the thin PANI containing layer, which constantly contacted

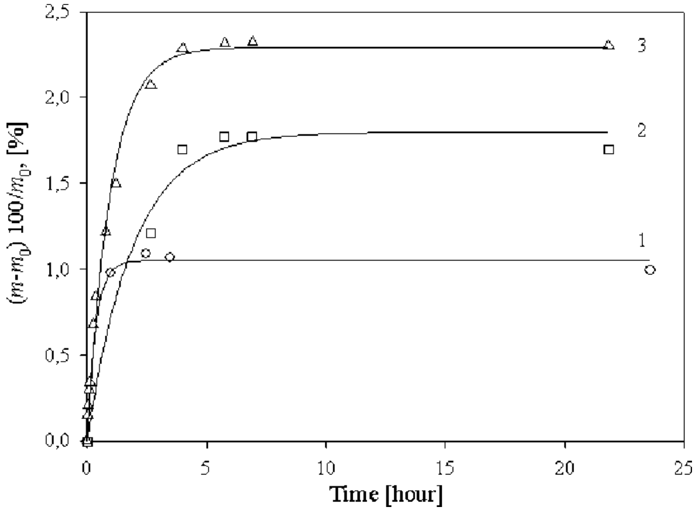

Fig. 4. Swelling kinetic curves of the PA-12 film in distilled water (*1*), in aqueous HCl solution (1 M) (*2*) and in 0.1 M $(NH_4)_2S_2O_8$ acidic (1 M HCl) water solution (*3*) (m_0 and m are the weight of the primary and the swelled films, respectively).

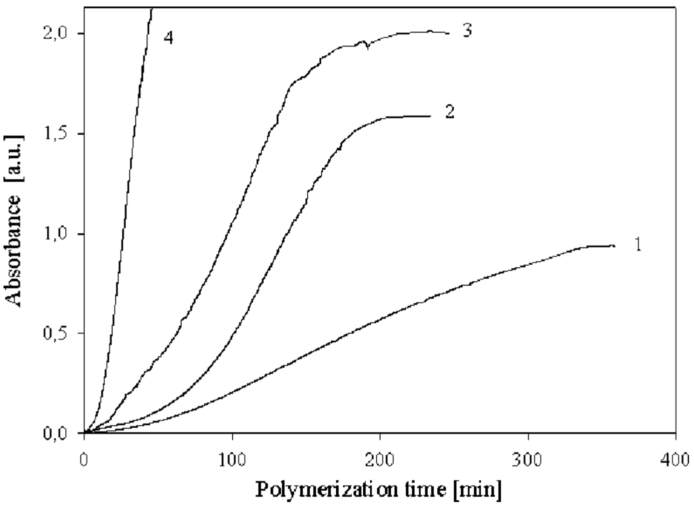

Fig. 5. Kinetic curves of PANI formation in the PA-12 film measured at 750 nm with the constant aniline content ($C_{aniline} = 0.56$ M): $C^{(NH_4)_2S_2O_8} = 0.1$ M (*1*); 0.15 M (*2*); 0.17 M (*3*); 0.2 M (*4*).

with the solution of the almost initial oxidant concentration* during the polymerization. In turn, this could cause deep oxidation and even overoxidation processes (25) that resulted in the deceleration of the matrix polymerization process and, correspondingly, in widening the exciton band to blue side of the spectrum (see above and Figure 3). At the same time, unlike the Nylon-6 case (22), we did not observe decoloration of the composite film with formed PANI. Only the darkening of this film to deep green was observed for long polymerization times.

Naturally, quantitative characteristics of the whole polymerization process (i.e., not only of the deceleration stage) depend both on the aniline concentration in the matrix and on the oxidant concentration in the solution. Specifically, this is confirmed with the kinetic profiles of the matrix aniline polymerization, which were obtained at different aniline and APS concentrations by monitoring changes of optical density of the exciton band at 750 nm (Figures 5 and 6). These dependencies have a pronounced S-shape, typical of the autocatalytic aniline polymerization in solution or matrix systems and testify to an existence of IP, the propagation stage and the deceleration/termination (degradation) stage (e.g. see (11, 23, 24)). However, it should be emphasized that the concentrations of aniline and APS in the system under investigation were in the ranges ~0.6–1.4 M (in the matrix) and 0.1–0.2 M (in the solution), respectively, i.e., much higher (by one–two orders of magnitude) than typically used in most of the known solution based mediums (19, 23, 24). However, despite this, in both cases, the values of IP were roughly in the same time range (~10–50 min) depending on concentrations of the reagents. This fact confirms the above-mentioned specificity of the matrix polymerization and slowness of formation of the transition state (rate determining step) in comparison with the solution based medium.

The difference between the matrix and solution based polymerization mediums can be seen also in a dependence of IP, slope and curvature of the kinetic curves on concentration of the reagents. Specifically, in the case of aniline polymerization in the presence of dodecylbenzenesulfonic acid in a water solution, Madathil et al. (24) displayed data, which allowed us to conclude that IP in this system decreased approximately by a factor of eight when doubling amount of

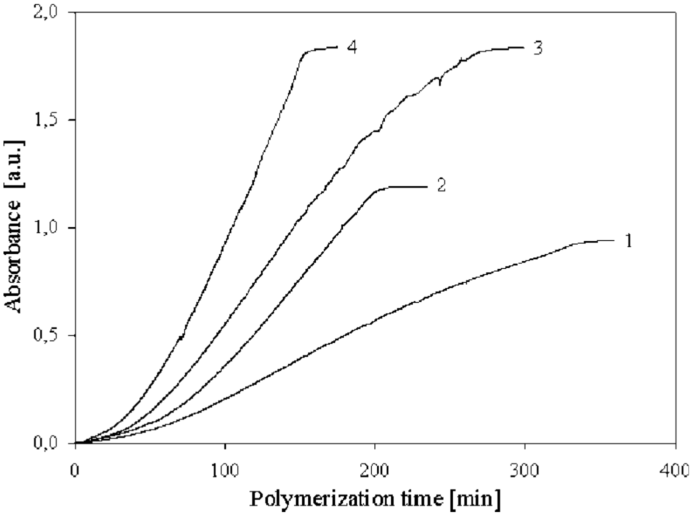

Fig. 6. Kinetic curves of the PANI formation in the PA-12 film measured at 750 nm with the constant oxidant concentration ($C^{(NH_4)_2S_2O_8} = 0.1$ M): $C_{aniline} = 0.56$ M (*1*); 0.81 M (*2*); 1.12 M (*3*); 1.36 M (*4*).

---

*The fact that the oxidant concentration kept on the practically initial level might be explained by the oxidant low consumption in the polymerization, which ran only in the thin layer of the matrix. This layer contained only a small part of total aniline quantity in the whole matrix.

APS. The slope of the kinetic curve part, which corresponded to the propagation stage, remained virtually unchanged. Such a result confirms the independence of the rate of the propagation stage on the oxidant concentration in this solution based system (24). On the contrary, in the aniline matrix polymerization we found much less change of the IP duration but a rise of slopes both of the IP and propagation step parts of the kinetic curve with increasing the oxidant concentration (Figure 5).

The significant increase of the aniline concentration in the matrix (from 0.56 M to 0.81 M) also insignificantly affected the IP duration. However, this increase led to more than a two-fold change of the slopes both of the IP and propagation parts of the kinetic curves i.e., to the growth of the rates of the IP and propagation steps (Figure 6). The increase of the aniline concentration to 1.12 M resulted in a complication of the kinetic curve shape that displayed changes probably in a condition of the swelled PA-12 matrix. Finally, when the aniline concentration in the matrix was increased to 1.36 M, the shape of the kinetic curve dramatically changed, which testified to a significant decrease of the IP duration and to an increase of the polymerization rate even without a termination step observing at the lower concentrations of aniline.

It is well known that the solution process includes homogeneous (in fact, this is IP) and heterogeneous (auto-acceleration step) stages, which have been described by two constants in the following kinetic Equation (19, 20, 23):

$$-\mathrm{d[AN]/dt} = k_1\mathrm{[AN][APS]} + k_2\mathrm{[AN][P]} \qquad (1)$$

where [AN], [APS] and [P] are concentrations of aniline, APS and PANI, respectively. $\boldsymbol{k_1}$, $\boldsymbol{k_2}$ are rate constants of homogeneous and heterogeneous stages. $\boldsymbol{k_2}$ is an observed complex rate constant including a contribution from the specific surface area of the precipitating PANI.

As one can see from Equation (1), in a typical solution medium, the homogeneous stage is determined by both aniline and oxidant concentrations, while the heterogeneous (dispersion and precipitate) one depends on aniline and PANI concentrations. However, as we discussed above, the case of the aniline matrix polymerization may be considered as a solid solution process with all products distributed in the matrix including even insoluble PANI*. This situation is probably closer to the solution polymerization of aniline derivatives e.g. of *N*-methylaniline (NMA), which results in formation of the soluble polymer - poly(*N*-methylaniline). Kinetics of this process in the solution was described by Sivakumar et al. (19), who used the simplified equation with only one constant:

$$\mathrm{R_p} = k\mathrm{[NMA]^2[PDS]} \qquad (2)$$

where [NMA] and [PDS] are concentrations of NMA and potassium peroxodisulfate, respectively. $\mathrm{R_p}$ is the rate of polymerization.

However, taking into account the found effects of the reagent concentrations on rates of all stages of the aniline matrix polymerization (Figures 5 and 6), one may deduce that the rate of this process could be described by Equation (3), which is more complicated than Equations (1) and (2).

$$\mathrm{R_p} = \mathrm{dP/dt} = k_1\mathrm{[AN]}^{x1}\mathrm{[APS]}^{y1} + k_2\mathrm{[AN]}^{x2}\mathrm{[APS]}^{y2}\mathrm{[P]}^{z} \qquad (3)$$

where x_1, x_2 and y_1, y_2 and z are reaction orders with respect to aniline, APS and P (PANI) concentrations, respectively. dP/dt is the rate of the PANI formation, which is determined on the basis of the technique of evaluation of the PANI quantity in the matrix (see the *Evaluation of the PANI Yield in the Composites* section). $\boldsymbol{k_1}$ and $\boldsymbol{k_2}$ are the rate constants of IP and propagation stages, respectively.

In order to evaluate the reaction orders $\boldsymbol{x_1}$ and $\boldsymbol{x_2}$ with respect to aniline, the kinetic curves of the PANI formation in the PA-12 film were obtained at a fixed APS concentration in the solution and different aniline concentrations in the film (Figure 6). It was found that values of $\boldsymbol{x_1}$ and $\boldsymbol{x_2}$ were both equal to ~3. These values are much higher than those found in the solution cases (equal to 1 or 2, see Equations (1) and (2) (19, 20, 23)) and confirm some specificity of the matrix polymerization.

As a possible reason for these increased reaction orders, one may consider that unlike the solution system, both stages of the polymerization process in the matrix involve the undiluted aniline localized in the free volume of the solid matrix (see the section *On Specificity of Aniline Matrix Polymerization*).

This also means that a real operating concentration of aniline in the reaction zones of the matrix is higher as compared with the calculated one. Indeed, the latter was calculated on the basis of the rough assumption of homogeneous aniline distribution in the entire matrix volume (see *Preparation of the PA-12/PANI Layered Composites*), whereas, in reality, it is distributed inside the free volume being a part of the matrix volume. Therefore, the determined high values of $\boldsymbol{x_1}$ and $\boldsymbol{x_2}$ orders may be considered only as preliminary and inflated values. These values will be redetermined later in a further work after measurements of the free volume of the PA-12 films containing different quantities of aniline.

Despite a growth of the matrix polymerization rate and total quantity of PANI formed in the matrix with the increase of aniline concentration, a PANI yield showed extreme behavior (Figure 7, curve 1). Specifically, when increasing the aniline concentration, the PANI yield smoothly grew from 49% to a maximum value of 60% at ~0.8 M of the aniline content, followed by its lowering to 47.7% for 1.36 M aniline (Figure 7, curve 1). This suggested some limitations in the aniline matrix polymerization due to the hindered penetration of the inorganic oxidant and acid ions from the solution into the reaction zone of the dielectric

---

*PANI in such systems is produced in a form of clusters (12, 13), which are probably localized in free volume voids where the monomer was initially accumulated.

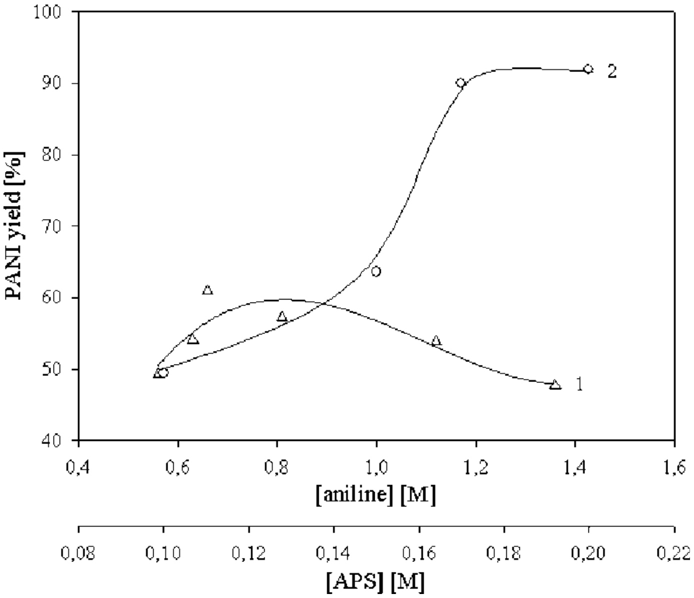

Fig. 7. Effect of the aniline (at $C(NH_4)_2S_2O_8 = 0.1$ M) (*1*) and APS (at $C_{\text{aniline}} = 0.56$ M) (2) concentration on the PANI yield in the PA-12 matrix film.

matrix. Indeed, the quantity of these penetrated reagents can be insufficient to polymerize the whole quantity of the monomer in the reaction zone. As a consequence, the efficiency of the matrix polymerization decreases after a critical aniline concentration, which in accord with the obtained data (Figure 7, curve 1) can be near 0.8 M.

The specificity of the aniline matrix polymerization consists also in the participation of APS, not only in the IP stage, but also in the propagation stage. The reaction orders y_1 and y_2 with respect to APS at fixed aniline concentration in the film and different oxidant concentrations in the solution were found to be ~ 2 and ~ 1, correspondingly, i.e. y_1 was two-fold higher than in the solution case (equal to 1, see Equations (1) and (2) (19, 20, 23)). Obviously, such an increase of the reaction order y_1 for the IP stage testifies to important changes in the oxidant interaction with aniline localized in the matrix as compared with the solution systems. Specifically, this may be explained to some extent by the fact that in the oxidizing solutions containing HCl and persulfate salt, the formation of chlorine proceeds that results in an additional consumption of the persulfate salt. Chlorine formation is followed by its hydrolysis to produce another oxidant HOCl, which is weakly dissociated and easily penetrates into the nonpolar matrix and then participates in the aniline polymerization (11). The same factor may lead to the indirect participation of APS in the second (propagation) step that resulted in its effect on the rate of this stage (Equation (3)).

Some circumstantial confirmation of the appearance of the additional oxidant in the solution may be obtained probably from the S-shape dependence of the PANI yield on APS concentration (Figure 7, curve 2). Specifically, there is a significant acceleration of the growth of the PANI yield from $\sim$64% till 90% at middle concentrations of APS (0.15–0.17 M) followed by the strong deceleration when the concentration is increased from 0.17 M to 0.2 M (Figure 7, curve 2). This development of the polymerization process at the middle concentrations of APS may be explained obviously by the appearance of the noticeable quantity of HOCl. But, its further deceleration at increased concentrations of APS can be caused probably by overoxidation of the forming PANI that leads to dropping surface conductivity of the formed composite from $\sim 10^{-5}$ S/sq to $\sim 10^{-8} - 10^{-9}$ S/sq.

The reaction order with respect to PANI (*z*, see Equation (3)), also has increased value ~ 1.5 in comparison with the one of the solution case (see Equation (1) and (20), 23)). Since it is difficult to explain clearly this fact at presentl, or to find possible reasons for increasing the value of *z*, we may consider the effect of physical-chemical interaction of PANI with the matrix on its activity in the polymerization process. This and other possibilities will be checked in a further work.

Rate constants k_1 and k_2 in Equation (3) were determined to be $0.076\ \text{mol}^{-4} \cdot \text{min}^{-1}$ and $0.202\ \text{mol}^{-4.5} \cdot \text{min}^{-1}$, respectively, i.e., in the matrix case these constants differed only by less than three times. On the other hand, the first one is about the same order but the second one is much lower than corresponding values of k_1 and k_2 of the solution polymerization process (20, 23). This strong kinetic dissimilarity in k_2 values between the matrix and solution processes is probably connected with a condition of a PANI dispersion phase forming in the both media. Specifically, an access of the monomer and oligomer molecules to the surface of PANI clusters, which are immobilized in the solid matrix, is impeded by strong diffusion limitations. As a consequence, a catalytic activity of these clusters cannot be effectively realized in the propagation stage unlike the known situation (20, 23) in the liquid mediums. This reason suggests that in the matrix case the surface factor of the kinetics of the aniline polymerization is practically excluded and the constant k_2 is the real rate constant while in the solution this constant is the observed one (23).

3.3 Raman Spectrometry

Figure 8 shows Raman spectra of the pure PANI powder and composite PA-12/PANI films in ES and EB oxidation states. To make a comparison, the figure also includes the spectrum of the parent PA-12 film. This spectrum contains bands assigned in accordance with (26) to: C-C stretching (1068 and 1114 cm^{-1}); stretching of carbonyl group (1640 cm^{-1}); N-H stretching (3297 cm^{-1}, not shown), C-N-H in plane bending (1558 cm^{-1}), as well as bands of CH_2–groups stretching (2852, 2889 and 2927 cm^{-1}, not shown) and in-phase-twisting mode of the CH_2–groups (1298 and 1440 cm^{-1}).

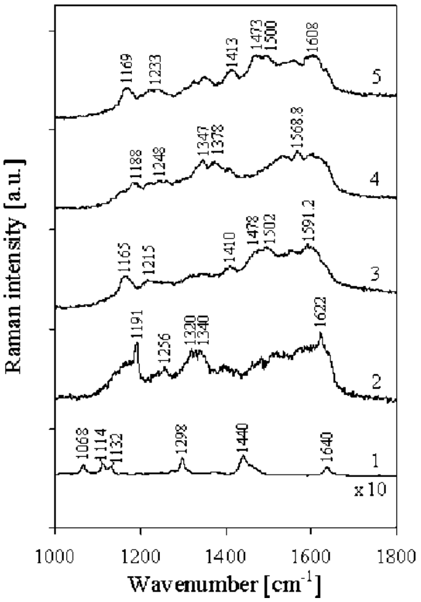

Fig. 8. Raman spectra of the PA-12 film (*1*), PANI in the form of ES (*2*) and EB (*3*), the composite PA-12/PANI film in doped (*4*) and dedoped (*5*) states.

In the spectrum of ES form of PANI (Figure 8, curve 2) the bands at 1622 cm^{-1} and at 1191 cm^{-1}, which are assigned to C=C stretching and C-H bending of benzenoid units, respectively, reveal the presence of the doped PANI structures (27). The band at 1256 cm^{-1} is characteristic of C-N stretching mode of polaron units (28). Moreover, the presence of the vibrational fine structure in the wavenumber region of 1320–1340 cm^{-1} can be attributed to the >C-N$^{+\bullet}$ stretching mode of delocalized polaron charge carriers (14). The presence of all these vibrational modes clearly proves that the formed PANi is in the conducting state.

In the case of the EB powder (Figure 8, curve 3) the Raman bands at 1165 cm^{-1} and 1410 cm^{-1} indicate the presence of the C-H deformation modes and the C-C stretching of the quinoid ring (27), respectively. The broad band at 1478–1502 cm^{-1} related to >C=N stretching (16) confirms that non-protonated quinoid segments are present in the EB powder. The band at 1215 cm^{-1} is the characteristic of >C-N- stretching in the benzenoid segments (26). As one can see, the characteristic polaron bands at 1256 cm^{-1} and at 1320–1340 cm^{-1} almost disappeared (none of the basic forms of PANI gives rise to vibrational modes in this spectral region). However, their minor intensities still testify to the presence of the dopant impurities in the EB sample.

In the case of Raman spectra of the composite PA-12/PANI films, only bands of PANI could be observed under the investigation conditions (see section, *Evaluation of the PANI Yield In The Composites*, Figures 1 and 7). Hence, after comparison of the Raman spectra of the composite film with those of pure PANI (Figure 8) we concluded that the spectra revealed the presence of the characteristic PANI bands. However, some of these bands in the case of the composite films shifted to the red region as compared to pure PANI (Figure 8). Specifically, in the spectrum of the doped sample the semi-quinone radical >C-N$^{+\bullet}$ band at 1320–1340 cm^{-1} significantly shifted towards 1347–1378 cm^{-1}. However, the dedoped sample (Figure 8, curve 5) showed only a negligible shift of the band at 1165 cm^{-1} (C-H deformation of the quinoid ring) to 1169 cm^{-1}, and the band at 1410 cm^{-1} (C-C stretching of the quinoid ring) to 1413 cm^{-1}. Obviously, such behavior confirms the above stated interaction of PANI with the matrix. On the other hand, this shifting testifies that the degree of interaction strongly depends on protonation of PANI, namely on the significant interaction of the radical cation fragments of the doped composite sample with electronodonor groups of the polyamide matrix and on practically negligible interaction in the case of the dedoped sample.

Taking into account the fact that PANI is formed in the doped state inside the matrix, one may infer that the above Raman data are evidence of the appearance of the physical-chemical interaction of the forming doped PANI with the matrix during the aniline polymerization. Obviously, this appearing interaction affects kinetic parameters of the aniline matrix polymerization in comparison with the process usually runs in the solution based system that is displayed by the increased orders of the kinetic Equation (3).

4 Conclusions

Composite PA-12/PANI films can be formed by a treatment of the PA-12 films swelled in aniline with water solution of APS and HCl. With the help of a specific adaptation of confocal micro-Raman Resonance spectrometry it was shown that the process of the aniline matrix polymerization is realized only in a very thin (2 μm) subsurface layer of the matrix. A combination of the Raman data with the UV–Vis spectroscopy based on own approach allowed determining the PANI concentrations and yield in this conductive layer. The data obtained were used as the quantitative basis to study kinetic peculiarities of the matrix polymerization process.

Similar to the known solution based aniline polymerization systems, chemical polymerization of aniline in the surface layers of the PA-12 matrix runs through stages of IP, propagation step and termination. However, kinetic, swelling and Raman spectrometry data suggest that this process in the matrix has a strong difference in comparison with the solution due to not only the physical-chemical interactions of aniline and formed PANI with amide groups of the matrix, but also to a physical state of aniline localized in voids of the free volume of the matrix.

From a kinetics position, this specificity results in an increase of the reaction orders with respect to reagents in the two-constant kinetic equation of the polymerization process and in a participation of APS in the propagation stage. Formation of the additional oxidant HOCl in the oxidizing solution due to oxidation of HCl by APS can have a partial effect on the matrix polymerization kinetics as well. Specifically, a diffusion penetration of this weakly dissociated oxidant into the dielectric polyamide matrix is obviously favored as compared with ionized APS.

The strong kinetic dissimilarity between the both processes is displayed also in much less value of rate constant k_2 of the propagation stage of the matrix as compared with the solution. Whereas, in the latter case, this constant is the observed value and includes a surface factor (23). One may assume that the difference in the k_2 values of the both processes are connected not only with the above interactions in the system, but also with a condition of a PANI dispersion phase formed in the solid matrix and solution media. Specifically, PANI clusters immobilized in the matrix cannot adsorb at their surface the monomer and oligomer molecules by diffusion limitations and correspondingly are unable to catalyze effectively the propagation stage, unlike the known situation (20, 23) in the solution medium. For this reason, we suggest that in the matrix case, the surface factor of the kinetics of the aniline polymerization is nearly excluded and the constant k_2 is a real rate constant.

5 Acknowledgements

K. Yu Fatyeyeva is grateful to the French government for financial support.

6 References

1. Bhattacharya, A. and De, A. (1996) *Prog. Solid State. Chem.*, **24(3)**, 141–181.
2. Anand, J., Palaniappan, S. and Sathyanarayna, D.N. (1998) *Prog. Polym. Sci.*, **23(6)**, 993–1018.
3. Pud, A., Ogurtsov, N., Korzhenko, A. and Shapoval, S. (2003) *Prog. Polym. Sci.*, **28(12)**, 1701–1753.
4. Zilberman, M., Siegmann, A. and Narkis, M. (2000) *J. Macromol. Sci. Phys., B*, **39(3)**, 333–347.
5. Titelman, G.I., Zilberman, M., Siegmann, A., Haba, Y. and Narkis, M. (1997) *J. Appl. Polym. Sci.*, **66(12)**, 2199–2208.
6. Zilberman, M., Siegmann, A. and Narkis, M. (1998) *J. Macromol. Sci. Phys., B*, **37(3)**, 301–318.
7. Koul, S., Chandra, R. and Dhawan, S.K. (2001) *Sens. and Actuators B*, **75(3)**, 151–159.
8. Fan, J., Wan, M. and Zhu, D. (1999) *Solid State Commun.*, **110(1)**, 57–62.
9. Gazotti, W.A., Jr., Faez, R. and De Paoli, M.-A. (1999) *Eur. Polym. J.*, **35(1)**, 35–40.
10. Byun, S.W. and Im, S.S. (1999) *Polymer*, **39(2)**, 485–489.
11. Pud, A.A., Rogalsky, S.P., Shapoval, G.S. and Korzhenko, A.A. (1999) *Synth. Met.*, **99(2)**, 175–179.
12. Pud, A.A., Tabellout, M., Kassiba, A., Korzhenko, A.A., Rogalsky, S.P., Shapoval, G.S., Houze, F., Schneegans, O. and Emery, J.R. (2001) *J. Mater. Sci.*, **36(14)**, 3355–3363.
13. Tabellout, M., Fatyeyeva, K., Baillif, P.-Y., Bardeau, J.-F. and Pud, A.A. (2005) *J. Non-Crystalline Solids*, **351(33–36)**, 2835–2841.
14. Furukawa, Y., Ueda, F., Hyodo, Y., Harada, I., Nakajima, T. and Kawagoe, T. (1988) *Macromolecules*, **21(5)**, 1297–1305.
15. Bernard, M.C., Bich, V.T. and Hugot-Le Goff, A. (1999) *Synth. Met.*, **101(1–3)**, 811–812.
16. Bernard, M.C. and Hugot-Le Goff, A. (1997) *Synth. Met.*, **85(1–3)**, 1145–1146.
17. MacDiarmid, A.G., Xia, Y.N. and Wiesinger, J.M. (1995) US patent 5 403 913.
18. Bodalia, R., Manzanares, J., Reiss, H. and Duran, R. (1994) *Macromolecules*, **27(8)**, 2002–2007.
19. Sivakumar, C., Gopalan, A., Vasudevan, T. and Wen, T.-C. (2002) *Synth. Met.*, **126(2–3)**, 123–135.
20. Gill, M.T., Chapman, S.E., DeArmitt, C.L., Baines, F.L., Dadswell, C.M., Stamper, J.G., Lawless, G.A., Billingham, N.C. and Armes, S.P. (1998) *Synth. Met.*, **93(3)**, 227–233.
21. Ayad, M.M., Germaey, A.H., Salahuddin, N. and Shenashin, M.A. (2003) *J. Colloid and Interface Sci.*, **263(1)**, 196–201.
22. Neoh, K.G., Tay, B.K. and Kang, E.T. (2000) *Polymer*, **41(1)**, 9–15.
23. Tzou, K. and Gregory, R.V. (1992) *Synth. Met.*, **47(3)**, 267–277.
24. Madathil, R., Ponrathnam, S. and Byrne, H.J. *Polymer*, 2004, **45(16)**, 5465–5471.
25. Pud, A.A. (1994) *Synth. Met.*, **66(1)**, 1–18.
26. Lin-Vien, D., Colthup, N.B., Fateley, W.G. and Grasselli, J.G. The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules; Academic Press: San Diego, 1991.
27. Pereira da Silva, J.E., Temperini, M.L.A. and Cordoba de Torresi, S.I. (1999) *Electrochimica Acta*, **44(12)**, 1887–1891.
28. Laska, J., Girault, R., Quillard, S., Louarn, G., Pron, A. and Lefrant, S. (1995) *Synth. Met.*, **75(1)**, 69–74.