Colloid Polym Sci 275:814–820 (1997)

ORIGINAL CONTRIBUTION

A. Riede
M. Helmstedt
V. Riede
J. Stejskal

Polyaniline dispersions 7. Dynamic light scattering study of particle formation

Received: 24 February 1997
Accepted: 7 May 1997

A. Riede (✉) · M. Helmstedt · V. Riede
Faculty of Physics and Geosciences
University of Leipzig
04103 Leipzig, Germany

J. Stejskal
Institute of Macromolecular Chemistry
Academy of Sciences of the Czech Republic
162 06 Prague 6, Czech Republic

Abstract When aniline is oxidized in the presence of colloidal silica, composite polyaniline–silica particles of submicrometer size are obtained. Dynamic light scattering was used to monitor the course of dispersion polymerization of aniline and the formation of particles. The increase of a hydrodynamic radius of particles was observed as polyaniline had been produced. Additional increase in particle size after polymerization has also been recorded. The rate of aniline polymerization was found to increase with increasing temperature in the range 0–50 °C. Well-defined particles are formed below 30 °C while above this temperature the colloidal stability of the resulting systems is limited. The activation energy of aniline polymerization was estimated.

Key words Dynamic light scattering – polyaniline – dispersions – dispersion polymerization – colloidal silica – submicrometer particles

Introduction

Polyaniline (PANI) is one of the important electrically conducting polymers [1, 2]. It exists in a variety of forms [3, 4] differing in the electrical and optical properties. It is prepared by the chemical or electrochemical oxidation of aniline. The course of aniline polymerization can be monitored by various physico–chemical methods. The spectrophotometric studies are most rewarding [5–8], because of color changes occurring during the oxidation of aniline [3, 4]. Since polymerization of aniline is an exothermic reaction, the solution calorimetry was used [5, 9] to study this process. Acidity changes allow to follow the polymerization by recording pH of reaction mixture [3, 10–12]. The formation of cation radicals during the polymerization of aniline has been observed by EPR spectroscopy [8, 13]. Potentiometric measurements [9, 14–16] or the determination of residual aniline in reaction mixture by gas chromatography [17] have also been used to monitor the formation of PANI.

Processing of PANI, especially in its conducting form, is difficult because of its insolubility in most solvents. The preparation and application of PANI dispersions may thus be helpful. When aniline is oxidized in the presene of a suitable steric stabilizer, such dispersions are obtained. These are composed of submicrometer PANI particles dispersed in an aqueous medium. Polymers, viz. poly (vinyl alcohol) [6, 18, 19], poly(vinyl alcohol-*co*-vinyl acetate) [20, 21], poly(*N*-vinylpyrrolidone) [19], poly(vinyl methyl ether) [22, 23] or inorganic particles, e.g. colloidal silica [24, 25], have been used for the steric stabilization.

Dynamic light scattering (DLS) is an efficient tool of the particle-size determination. In case of PANI, it has been used to determine the hydrodynamic radius of particles in dispersions [18, 19, 24] and also to characterize the individual PANI macromolecules [26, 27]. In this paper we use DLS to investigate the dispersion polymerization of aniline in the presence of colloidal silica, and the formation of PANI–silica particles that are born during this process.

Experimental

Dispersion polymerization of aniline

Aniline hydrochloride (259 mg, 2 mmol) was dissolved in 6.8 ml of distilled water and 1 ml of colloidal silica (40 wt% aqueous suspension Ludox AS-40; Aldrich) was added. The solution was thermostated to desired temperature (0–50 °C) and 2 ml of 1 M aqueous solution of ammonium peroxydisulfate of the same temperature was introduced to start the oxidative polymerization of aniline [24]. The concentrations thus were: 0.2 M aniline hydrochloride, 0.2 M ammonium peroxydisulphate, and 0.05 g/ml of colloidal silica. The mixture was briefly stirred and then kept at rest during the following reaction [19].

Dynamic light scattering

Absorption of light by PANI in the visible region prevents a direct obervation of scattered light during polymerization. Therefore, 10 μl of the reaction mixture was diluted with 10 ml of water each 60 s and the diluted mixture was then immediately characterized by DLS. Polymerization was stopped at this low concentration of the reactants and the diluted mixtures were stable during measurement.

The light-scattering measurements were carried out at 25.0 $\pm$ 0.1 °C by a DLS-SLS-5000 Laser Light-Scattering Spectrometer/Goniometer (ALV, Germany) equipped with a Nd : YAG laser DPY 315 II (λ_0 = 532 nm, ADLAS, Germany) and a Multiple Tau Digital Correlator ALV-5000. The intensity autocorrelation function $G_2(t)$ was measured at an angle of observation of 90°. The field autocorrelation function $g_1(t)$ was determined from the intensity autocorrelation function by the relations $G_2(t) = A[1 + B\, g_1^2(t)]$ and $G_2(t) = \langle I(0)\, I(t)\rangle$, where A is the average uncorrelated scattering intensity, B is an instrument parameter and $I(0)$, $I(t)$ are the intensities at the time 0 and t, respectively. For small monodisperse particles, $g_1(t) = \exp(-\Gamma t) = \exp(-D_t q^2 t)$, where $q = (4\pi n/\lambda_0)\sin(\Theta/2)$ is the scattering vector, D_t the translational diffusion coefficient, Γ the decay rate, n the refractive index of the solvent, λ_0 the wavelength of the incident light *in vacuo*, and Θ the angle of observation. Real dispersions particles are never completely monodisperse and the superposition of their exponential functions is obtained. By Laplace inversion of $g_1(t)$ using the program CONTIN [28] provided by the ALV, the z-average of the distribution of translational diffusion coefficients is evaluated. The hydrodynamic radius R_h of the particles and macromolecules can be calculated from the translational diffusion coefficient D_t by the Stokes–Einstein equation, $D_t = kT/6\pi\eta_0 R_h$, where k is Boltzmann constant, T is the temperature and η_0 the viscosity of solvent [29], assuming their spherical shape. In order to characterize the polydispersity σ^*, we used the relative width of the radius distribution. This parameter is defined as the second moment or variance of the distribution in a logarithmic scale.

UV/VIS/NIR spectroscopy

The spectra of diluted dispersions were recorded with a UV/VIS/NIR spectrometer Lambda 19 (Perkin–Elmer). The absorption coefficient, α, of PANI was calculated from the optical transmission, $t_\lambda = t_0 \exp(-\alpha d)$, where d is the thickness of the cell. The parameter t_0 is the experimental transmission coefficient of all components of the reaction mixture with the exception of aniline hydrochloride.

Results and discussion

Dispersion polymerization has been often used to prepare polymer particles in submicrometer and micrometer range [30, 31]. In such polymerization, the monomer is miscible with the reaction medium, but the resulting polymer is insoluble under the same conditions. The macroscopic precipitation is prevented by the presence of the steric stabilizer. It has been recently observed that colloidal silica can be used for the stabilization [32, 33] of polyaniline dispersion and well-defined composite particles are produced [24] (Fig. 1).

We asssume that the formation of polyaniline–silica particles proceeds as follows: At the beginning of polymerization, the colloidal silica particles (steric stabilizer) are present in the reaction mixture (Fig. 2a). Polyaniline macromolecules formed during polymerization (Fig. 2b) aggregate into small primary particles and get attached to the steric stabilizer either by chemical grafting or by physical adsorption (Fig. 2c). Silica particles become partly or completely covered by the precipitating PANI and are "glued" together with PANI into much larger dispersion particles (Fig. 2d) [34]. A part of small ultrafine silica particles may still be free and not attached to the dispersion particles (Figs. 1 and 2d). The aggregation process is responsible for the "raspberry" morphology of the resulting particles [32, 33]. The final size of particles is dependent on the amount of PANI produced and on the concentration of stabilizer [24]. It will also be controlled by the thermodynamic balance between the attractive forces of the precipitating polyaniline macromolecules on the one hand and dissipative forces exerted on aggregates by the

Colloid & Polymer Science, Vol. 275, No. 9 (1997)

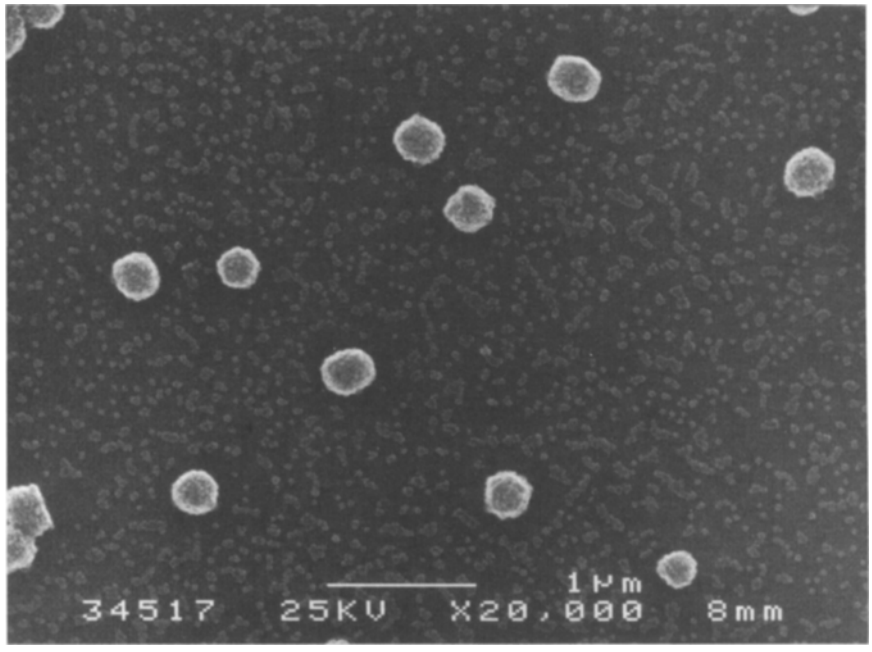


Fig. 1 Scanning electron micrograph of composite polyaniline–silica dispersion particles produced in dispersion polymerization of aniline at 0 °C. The unattached silica can be seen on the background

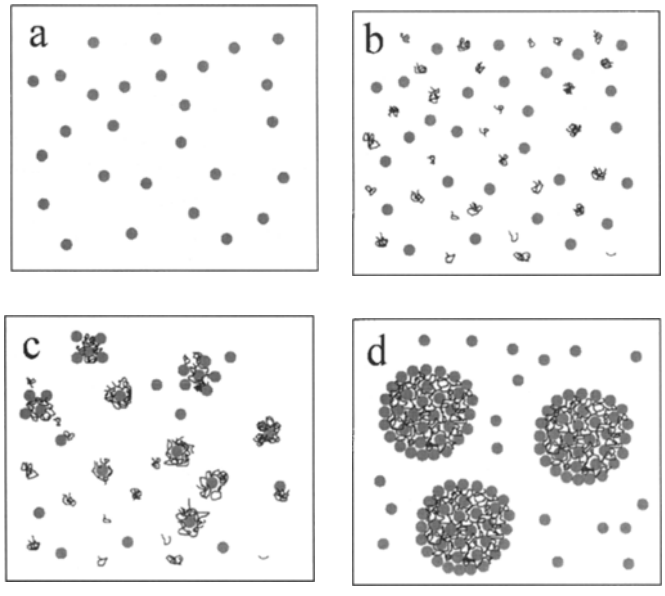


Fig. 2 Model of the formation of the composite PANI–silica particle produced in dispersion polymerization of aniline in the presence of colloidal silica: Particles of stabilizer, colloidal silica (a), get in contact with the PANI produced during polymerization (b) and nuclei of the future particles are produced by mutual interaction (c). The silica particles becomes glued by PANI to produce the final dispersion particles (d)

attached stabilizer on the other. This concept of particle formation is discussed in relation to results obtained by monitoring the dispersion polymerization of aniline in the presence of colloidal silica by DLS.

Dynamic light scattering

The dependence of the hydrodynamic radius of dispersion particles produced during polymerization on reaction time has a sigmoidal shape (Fig. 3a). During the induction period the reaction mixture is colorless. The DLS measurement is disturbed by occasional fluctuations of scattered light (not shown in Fig. 3c). The intensity of scattered light sharply increased for short moments (>1000 kHz for < 0.1 s), like if large objects were passing through the scattering volume. As the intensity was nearly constant at the beginning of the experiment ($t \approx 0$) this effect cannot be attributed to the presence of dust particles. We assume that these disturbances could have been caused by oxygen microbubbles resulting from decomposition of hydrogen peroxide produced in the reaction of ammonium peroxydisulfate with organic compounds in the system. The fluctuations of scattered light disappear after the polymerization has started. We have evaluated the hydrodynamic radius from the short measuring time with no fluctuations. The hydrodynamic radius was determined with a large error but roughly corresponded to the original silica particles measured separately ($R_h = 16$ nm, $\sigma^* = 0.01$). The polydispersity cannot be reliably determined by DLS (Fig. 3b).

At the onset of polymerization, the polydispersity of the system is high (Fig. 3b) and the nucleation of the future particles takes place. Although the nucleation probably determines the number of dispersion particles in the system, and is of fundamental importance, its nature is not completely understood. During the following particle

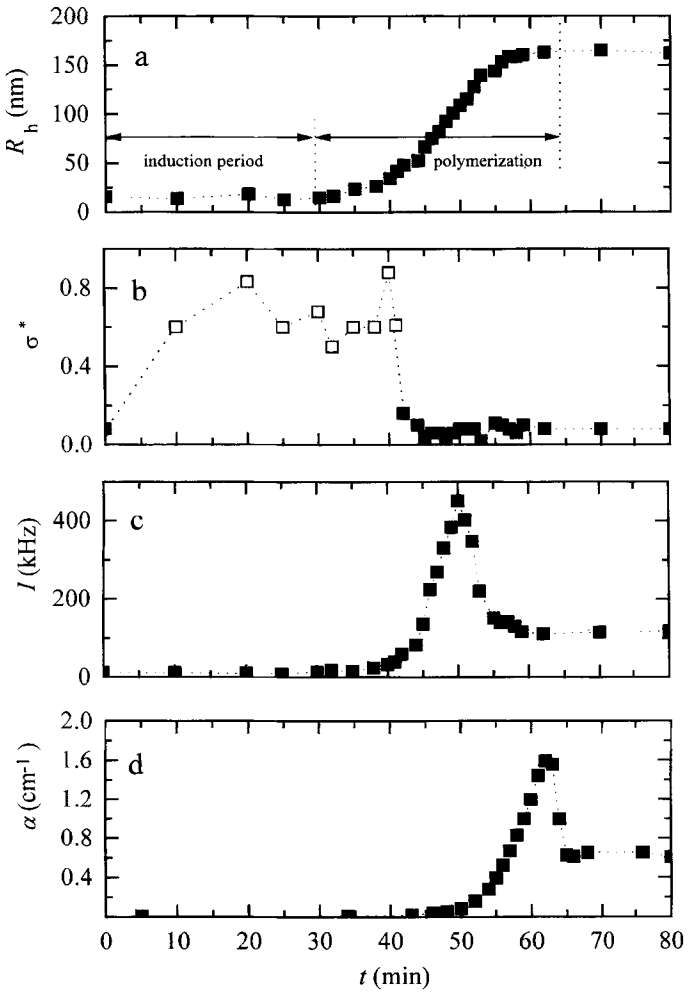


Fig. 3 The dependence of (a) hydrodynamic radius of particles, R_h, (b) polydispersity of particles characterized by relative width of the radius distribution, σ^*, (c) intensity of scattered light (count rate), I, and (d) the absorption coefficient, α (both at $\lambda_0 = 532$ nm), during the polymerization of aniline in the presence of colloidal silica at 0 °C

formation, the relative width of the radius distribution is low. It means that the number of particles produced at nucleation stage does not significantly change during subsequent polymerization, and the particles grow as the polymerization proceeds. The increase of the hydrodynamic radius is probably a linear function of time. Consequently, the amount of PANI produced in polymerization increases with the third power of polymerization time, in agreement with the well-established autoacceleration mechanism of this process [10, 17]. As mass of particles becomes larger, the intensity of scattered light increases at first (Fig. 3c). The second effect that controls the amount of the scattered light is its absorption by PANI. Due to the deep blue coloration of the reaction mixture during polymerization, even after dilution, the absorption of laser light at wavelength of 532 nm becomes significant (Fig. 3d). The primary beam and the scattered light become absorbed and the observed intensity of scattered light passes through a maximum and decreases (Fig. 3c).

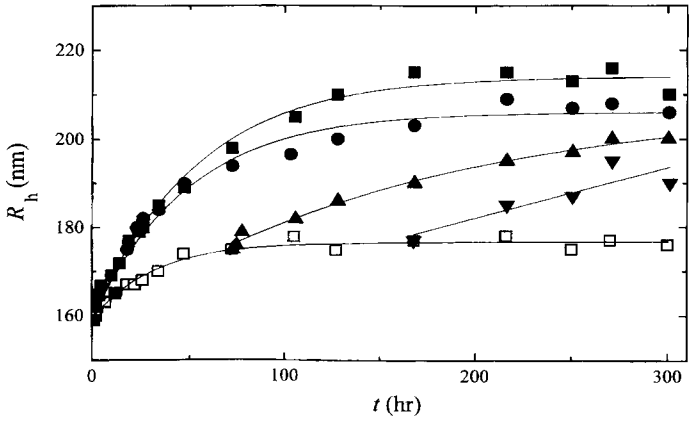
At the end of polymerization, the color of the reaction mixture turns from blue to green [3, 4]. The absorption of the green laser light becomes lower (Fig. 3d) and the intensity of scattered light stops to decrease (Fig. 3c).

Additional slow changes in particle size

Polymerization of aniline is typically completed in less than 1 h (Fig. 3) under the reaction conditions used in the present study and no additional changes in particle size or uniformity have been observed on this time scale. When, however, the dispersion particles prepared at 0 °C were left longer at this temperature, a small but well-reproducible increase in the hydrodynamic radius, from 160 to 186 nm, has been observed (Fig. 4, open symbols). We assume that this effect reflects the formation of the final overlayer of silica particles [32, 33] on the surface of a dispersion particle, especially in the places where PANI macromolecules are exposed to the dispersion medium.

If, during this ageing, a part of the dispersions was separated and further stored at 25 °C, additional irreversible increase in the particle size was observed to proceed on a similar time scale (Fig. 4, full points). The colloidal silica incorporated inside the composite particles has a tendency to get surrouded by molecules of water and the volume of the particles may increase. The swelling may be accompanied by the reorganization of the inner particle

Fig. 4 Changes of the hydrodynamic radius of the particles, R_h, kept at 0 °C (□) and at 25 °C after 1 (■), 12 (●), 70 (▲), 170 (▼) h at 0 °C. Data were fitted by an exponential growing function



Colloid & Polymer Science, Vol. 275, No. 9 (1997)

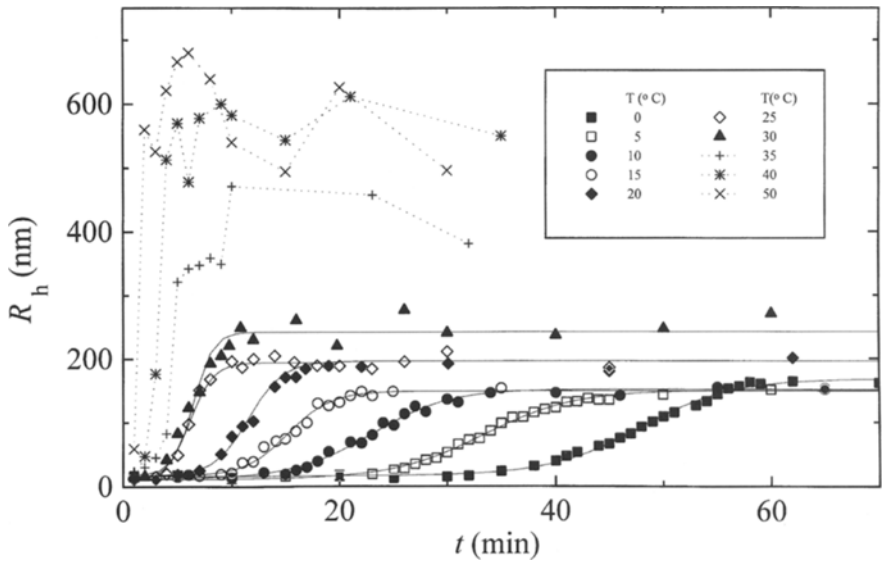


Fig. 5 The time dependence of the hydrodynamic radius, R_h, during the dispersion polymerization of aniline in the presence of colloidal silica at various temperature. The data for polymerizations at 0–30 °C were fitted with the sigmoidal function given by Eq. (1)

structure, which is then responsible for the irreversibility of the observed effect. In practice, both processes, formation of an overlayer and swelling, superimpose.

After the changes outlined above, the particle size remains constant and the dispersions are colloidally stable over the period of months and years. The easy sedimentation of particles (due to the high density of silica, 2.17 g cm^{-3}) does not cause any aggregation and PANI–silica dispersions can be recovered by gentle shaking.

Temperature dependence of polymerization

When the polymerization proceeds above 30 °C, the rate of polyaniline formation is high and time dependences of the hydrodynamic radius become disordered (Fig. 5). We assume that the diffusion processes are not fast enough to accommodate all PANI chains into well-defined dispersion particles. This is followed by uncontrolled aggregation of PANI, resulting in less organized [24] and polydisperse particles and even in the macroscopic precipitation of the product. It has been earlier reported that, besides the temperature change, the rate of polyaniline formation can be increased by addition of small quantities of substituted phenylenediamines [11] (one percent relative to aniline and less). When the rate of polyaniline formation had been increased by addition of such compound, the dispersion particles were not formed and only precipitates or gel-like structures were obtained. The high rate of aniline polymerization thus hinders the formation of well-defined particles in this case also. Below 30 °C, the rate of the reaction decreases with decreasing temperature (Fig. 5) and dispersion particles are produced. To sum up, the formation of the dispersion particle is influenced both by the thermodynamic (equilibrium) and dynamic (transport) effects.

The dispersion polymerizations of aniline made at various temperatures can produce some information on the rate of polyaniline polymerization. The shape of the time dependences of the hydrodynamic radii is sigmoidal and can be approximated by

$$R_h(t) = (R_d - R_s)[1 + \exp(t - t_0)g] + R_d, \quad (1)$$

where R_s is the hydrodynamic radius of the stabilizer, R_d of the final particles, g is a parameter related to the steepness of the function, and t_0 is the position of the inflection point.

From the sigmoidal fit, one can estimate duration of the induction period, t_i, and the polymerization time, t_p (Fig. 6). In the present analysis, we have defined the start of polymerization, t_i, as the time when the sigmoidal fit deviated from the radius of the steric stabilizer R_s for 1 nm and the end of polymerization, t_e, as the point where the sigmoidal fit differed for less than 1 nm from the final value of the particle size, R_d. The times t_i and t_e found in this way corresponded in the best way to the onset of the blue coloration at the start of polymerization and to the blue-to-green transition typical for its end. The time, needed for the formation of the particles can be taken as being equal to the polymerization time (Figs. 3a and d). Hence, the time of polymerization is defined as $t_p = t_e - t_i$.

The oxidation reaction of aniline can be divided into two parts: (1) The induction period, during which only the reactions of low-molecular-weight components take place and (2) the polymerization, in which PANI is produced. The rate constant of both processes is (at a given concentration of reaction components) proportional to the reaction velocity; the latter quantity can be taken as being

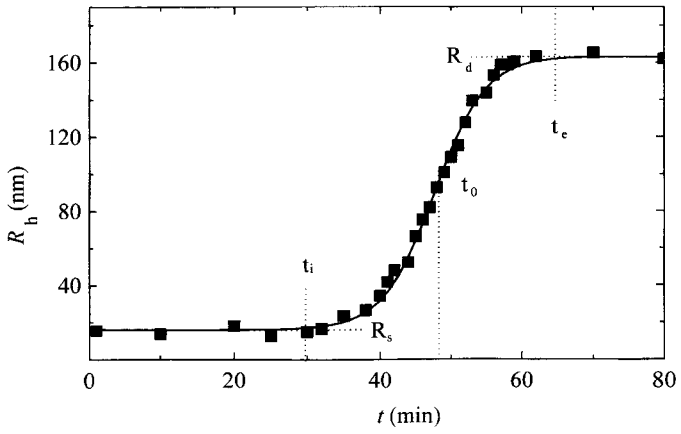


Fig. 6 The determination of the induction period, t_i, and polymerization time, $t_p = t_e - t_i$, from the time dependence of the hydrodynamic radius, R_h, by sigmoidal fit according to Eq. (1). Data for the polymerization at 0 °C are used for illustration

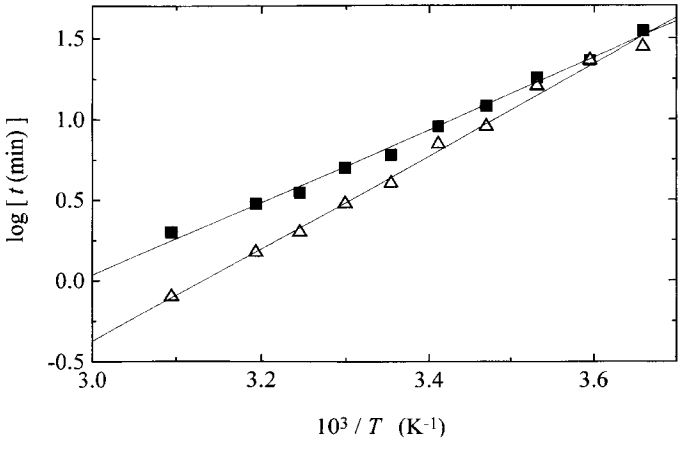


Fig. 7 The dependence of the induction period, $t = t_i$ (△), and of the polymerization time, $t = t_p$ (■), on the reciprocal temperture, $1/T$

proportional to the reciprocal value of time needed for completion of the individual reactions. By plotting the logarithm of the induction period, t_i, or of the polymerization time, t_p, vs the reciprocal temperature a linear dependence is obtained (Fig. 7). From this analogy of Arrhenius plot we may thus expect the slope of such dependence to be $E_A/2.303\ R$, where E_A is activation energy and $R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$ is gas constant. By analysis of the data we estimate the activation energy of the chemical processes during the induction period to be $E_{ai} = 54.8\ \text{kJ mol}^{-1}$, and the activation energy of the polymerization, $E_{ap} = 42.8\ \text{kJ mol}^{-1}$. These are larger than the activation energies for additions of radicals occurring during polymerization, e.g., of olefins [35], $E_A = 10$–$30\ \text{kJ mol}^{-1}$, and comparable to that of the generation of free radicals by decomposition of peroxydisulfates [35], $E_A = 50$–$60\ \text{kJ mol}^{-1}$.

Conclusions

The dynamic light scattering proved to be an efficient tool for the investigation of dispersion polymerization of aniline. The composite polyaniline–silica particle of submicrometer size is obtained when the oxidation of aniline is made in the presence of colloidal silica. After an induction period, polymerization of aniline starts and nuclei of future particle are formed. The hydrodynamic radius of particles increases as polyaniline is produced during the deep-blue stage of the polymerization process. After polymerization has been completed, additional changes in particle size have been observed. These are attributed to the perfection of the particle surface and to the swelling.

When the dispersion polymerization of polyaniline is carried out at temperature 0–25 °C, polyaniline–silica particles have a narrow distribution of sizes. When temperature exceeds 30 °C, the formation of polyaniline becomes too fast and the accommodation of the product into well-defined dispersion particles is not possible. In that case polydisperse particles with limited colloidal stability are obtained.

Acknowledgments The financial support of the Deutsche Forschungsgemeinschaft (Project No. He 2123/2-2 and 436 TSE 113/6 and of the Grant Agency of the Czech Republic (203/95/1297) is gratefully acknowleged.

References

1. Geniès EM, Boyle A, Lapkowski M, Tsintavis C (1990) Synth Met 36:139
2. Syed AA, Dinesan MK (1991) Talanta 38:815
3. Stejskal J, Kratochvíl P, Jenkins AD (1995) Collect Czech Chem Commun 60:1747
4. Stejskal J, Kratochvíl P, Jenkins AD (1996) Polymer 37:367
5. Fu Y, Elsenbaumer RL (1994) Chem Mater 6:671
6. Stejskal J, Kratochvíl P, Radhakrishnan N (1993) Synt Met 61:225
7. Gospodinova N, Mokreva P, Terlemezyan L (1993) Polymer 34:1330
8. Kobryanskii VM, Arnautov SA, Motyakin MV (1995) Vysomol soed A 37:35
9. Fong Y, Schlenoff JB (1995) Polymer 36:639
10. Stejskal J, Kratochvíl P, Špírková M (1994) Acta Polym 45:385
11. Stejskal J, Kratochvíl P, Špírková M (1995) Polymer 36:4135
12. Gospodinova N, Mokreva P, Terlemezyan L (1993) Polymer 34:2348

13. Kulikov AV, Kogan YL, Fokeeva LS (1993) Synth Met 55–57:1023
14. Wei Y, Hsueh KF, Jang GW (1994) Polymer 35:3572
15. Mattoso LHC, MacDiarmid AG, Epstein AJ (1994) Synth Met 68:1
16. Mahonar SK, MacDiarmid AG, Epstein AJ (1991) Synth Met 41–43: 711
17. Tzou K, Gregory RV (1992) Synth Met 47:267
18. Stejskal J, Kratochvíl P, Gospodinova N, Terlemezyan L, Mokreva P (1993) Polym Int 32:401
19. Stejskal J, Kratochvíl P, Helmstedt M (1996) Langmuir 12:3389
20. Stejskal J, Kratochvíl P, Gospodinova N, Terlemezyan L, Mokreva P (1992) Polymer 33:4857
21. Gospodinova N, Mokreva P, Terlemezyan L (1992) J Chem Soc Chem Commun 923
22. Banerjee P, Bhattacharyya SN, Mandal BM (1995) Langmuir 11:2414
23. Banerjee P, Mandal BM (1995) Macromolecules 28:3940
24. Stejskal J, Kratochvíl P, Armes SP, Lascelles SF, Riede A, Helmstedt M, Prokeš J, Křivka I (1996) Macromolecules 29:6814
25. Gill M, Baines FL, Armes SP (1993) Synth Met 55–57:1029
26. Davied S, Nicolau YF, Melis F, Revillon A (1995) Synth Met 69:125
27. Gettinger CL, Heeger AJ, Pine DJ, Cao Y (1995) Synth Met 74:81
28. Provencher SW (1982) Comput Phys Commun 27:213, 229
29. Brown W (ed) (1993) Dynamic Light Scattering/The Method and Some Applications. Clarendon Press, Oxford
30. Barrett KEJ (ed) (1975) Dispersion Polymerization in Organic Media. Wiley, London
31. Napper DH (1983) Polymeric Stabilization of Colloidal Dispersions. Academic Press, London
32. Maeda S, Gill M, Armes SP, Fletcher IW (1995) Langmuir 11:1899
33. Maeda S, Armes SP (1994) J Mater Chem 4:935
34. Markham G, Obey TM, Vincent B (1990) Colloids Surf 51:239
35. Tedder JM, Cooper W (1974) In: Jenkins AD, Ledwith A (eds) Reactivity, Mechanism and Structure in Polymer Chemistry. Wiley, London, pp 40–43, 182