

Ionic processes in irradiated solid polymers

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Abstract The reactions of ionic species generated in irradiated polymers (polyethylene, poly(dimethylsiloxane), poly(methyl methacrylate), and poly(ethylene terephthalate)) doped with pyrene, Py, were observed by radiothermoluminescence and complementary absorption spectroscopic measurements. The charge stabilization in polymers and charge transfer to the solute depend on the chemical structure of polymer chains and physical state of the polymer matrix. The recombination of ionic species is stimulated by relaxation processes of polymers. Total neutralization of charges in irradiated polymers occurs at the glass transition temperature of polymers. Mutual recombination of Py radical ions generates singlet excited states of the solute followed by Py monomer and excimer (depending on the solute concentration) fluorescence. Recombination of Py radical cations and negative species from the polymer matrix leads to the formation of Py triplet excited states followed by Py phosphorescence.

Key words irradiated polymers • radical ions • ion recombination • radiothermoluminescence • relaxation phenomena in polymers

Introduction

Polymeric solids have been widely used as resist, imaging, coating, and opto-electrical materials in contemporary industry and our daily life. The performance of this category of polymers is essentially determined by their response to radiation action [25]. High energy irradiation of polymers leads to efficient production of excited states and primary charges: positive holes and electrons. Primary charges can recombine and generate excited states of polymer molecules or undergo stabilization in polymer traps. Commercial polymers contain different types of additives which allow to modify their properties. Addition of solutes leads to scavenging of charges trapped in the polymer matrix and simultaneous formation of solute radical ions.

Pulse radiolysis followed by absorption and emission spectroscopy provides information concerning formation of excited states and charges in irradiated solid polymers in a short-time scale, ns- μ s [11, 24]. Investigations of the charge trapping in the most popular polymers: polyethylene (PE), poly(dimethylsiloxane) (PDMS), poly(methyl methacrylate) (PMMA), and poly(ethylene terephthalate) (PET), were performed in our laboratory during recent several years [12–14, 20].

Pulse radiolysis and ESR studies showed that primary charges can be stabilized in dopant free polymers in physical traps (PE, [3, 20, 21]) or in chemical traps (PMMA [6, 8, 9, 13, 22], PET [14]) as radical ions. Polymer radical anions were produced due to high

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Received: 3 January 2005
Accepted: 9 June 2005

positive electron affinity (EA) of atoms or chromophore groups in the polymer chain [11]. Charge transfer from polymer traps to solute molecules depends on chemical structure and physical state of the polymer matrix [11]. The ionic product reactions occurred according to diffusion mechanism at temperatures higher than the glass transition temperature (T_g) [12, 20]. Above T_g , recombination of solute radical ions generated monomer and excimer fluorescence of the admixture. At lower temperatures, below T_g , very small activation energy of the decay of ionic products (*ca.* 1–2 kJ·mol⁻¹) suggested that the tunnelling mechanism was involved [12–14, 20].

Using the technique of wavelength selected radiothermoluminescence (wsRTL) and complementary absorption spectroscopic measurements we investigated charge recombination processes in polymers doped with aromatic molecules [15, 16, 18, 19]. Pyrene, Py, was chosen as a spectroscopic probe because its radical ions, radicals, and singlet and triplet excited states are spectroscopically well characterized. The aim of this paper was to summarize the results of our studies [15–19] concerning the features controlling the ionic reactions in solid polymers in the long-time range (minutes) after irradiation. Using Py as the molecular probe in all investigated systems allowed to compare the ionic events in different polymers.

Sample preparation

The polymer samples were prepared as transparent films, *ca.* 0.5±1 mm thick. The way of the probe introduction into polymer samples was dependent on the physical properties of the polymer. Pyrene, Py, was introduced into polymer films either from the Py vapors (PE, PDMS) via vacuum sublimation at ambient temperature or from the Py solution in n-hexane or methanol (PE, PET) by immersing the polymer film in the solution. In order to introduce Py into PET film, the samples were boiled in Py-methanol solution, because Py molecules did not diffuse into PET film at room temperature. Afterwards, the polymer films were rinsed with the appropriate solvent to remove traces of Py molecules from the film surface and dried in a vacuum to remove any traces of the solvent as well as oxygen. In this way, the probe molecules were introduced into free volume of the polymer amorphous regions. Probe distribution was non-homogeneous and one can expect local aggregation of Py molecules depending on the polymer local free volume. This conclusion arises from the fact that the temperature dependences of the first half-life of the Py radical anion decay in the PDMS and PE matrices were well approximated by the Williams-Landel-Ferry equation [11, 19]. The free volume theory has been used successfully to describe diffusion of small molecules in polymers [23].

The PMMA-Py samples were prepared by the radiation induced polymerization of deaerated methyl methacrylate solutions containing Py.

The concentration of Py in all polymer films was determined spectrophotometrically, using the molar extinction coefficient equal to 11,500 dm³·mol⁻¹·cm⁻¹

at 308 nm. The irradiations were carried out at a temperature of 77 K with a few 4-μs pulses of linear accelerator (ELU-6, USSR-made). The total dose was kept within 4–6.5 kGy. More details concerning the experimental techniques can be found in original papers [15–19].

Results

The emission and absorption spectra recorded at 77 K for irradiated (77 K) polymer-Py films are shown in Fig. 1. The isothermal luminescence (ITL) from PE, PDMS and PMMA, all doped with Py (concentration range 5×10^{-3} – 5×10^{-2} mol·dm⁻³), exhibits strong monomer fluorescence of Py with the maximum at 395 nm and very weak emission in the 600–650 nm range, where Py phosphorescence was observed (Fig. 1A,B,C). Two strong absorption bands at $\lambda_{\max} \approx 450$ nm and $\lambda_{\max} \approx 490$ –500 nm assigned to Py^{•+} radical cation and Py^{•-} radical anion, respectively, were observed in these systems (Fig. 1A,B,C inserts). Emission of PET doped with Py ($\sim 1.3 \times 10^{-1}$ mol·dm⁻³) (Fig. 1D) consists of a wide band at $\lambda_{\max} \approx 475$ –500 nm with the shoulder at *ca.* 600 nm where phosphorescence bands of PET [7] and Py, respectively, were observed [18]. The lack of Py monomer fluorescence can be explained if one takes into account that for a high solute concentration the strong local aggregation of Py molecules can be expected. The Py monomer emission can be replaced by the excimer fluorescence originated from Py microcrystals formed at high Py content in PET. The Py excimer fluorescence band with the maximum at $\lambda_{\max} = 475$ nm cannot be observed separately because it is overlapped by PET phosphorescence.

The absorption spectrum of PET containing $\sim 1.3 \times 10^{-1}$ mol·dm⁻³ Py (Fig. 1D insert) shows the Py^{•+} band at 450 nm but the Py^{•-} peak at 490–500 nm is overlapped by the absorption band in the range 500–530 nm assigned to PET^{•-} radical anion [14]. In the PET-Py system electron transfer from the matrix radical anion (PET^{•-}) to Py seems to be unfavourable. The EA values of solid polymers seem to be unknown. However, the relative EA values found for different solutes in the 2-methyltetrahydrofuran glass: 0.14 eV for methyl methacrylate, 1.24 eV for phthalic anhydride (model compound for PET) and 0.63 eV for Py [1], suggest that the electron transfer between PMMA^{•-} radical anion and Py is probable, but that between PET^{•-} and Py is rather impossible. One can suppose that emission observed in the PET-Py system followed the recombination of Py^{•+} radical cations and PET^{•-} radical anions. The luminescence detected at 77K occurs due to charge recombination via tunnelling [5].

The absorption spectra of irradiated (77 K) polymer-Py systems detected during warming up the samples to room temperature are presented in Fig. 2. When temperature rises up the intensities of absorption bands of Py radical ions decrease. In PE-Py (Fig. 2A) and PDMS-Py (Fig. 2B) systems both Py radical ion bands disappeared completely at temperatures close to T_g of the polymer matrix [2, 4]. Also, the wsRTL peaks for these systems were found in the temperature range where

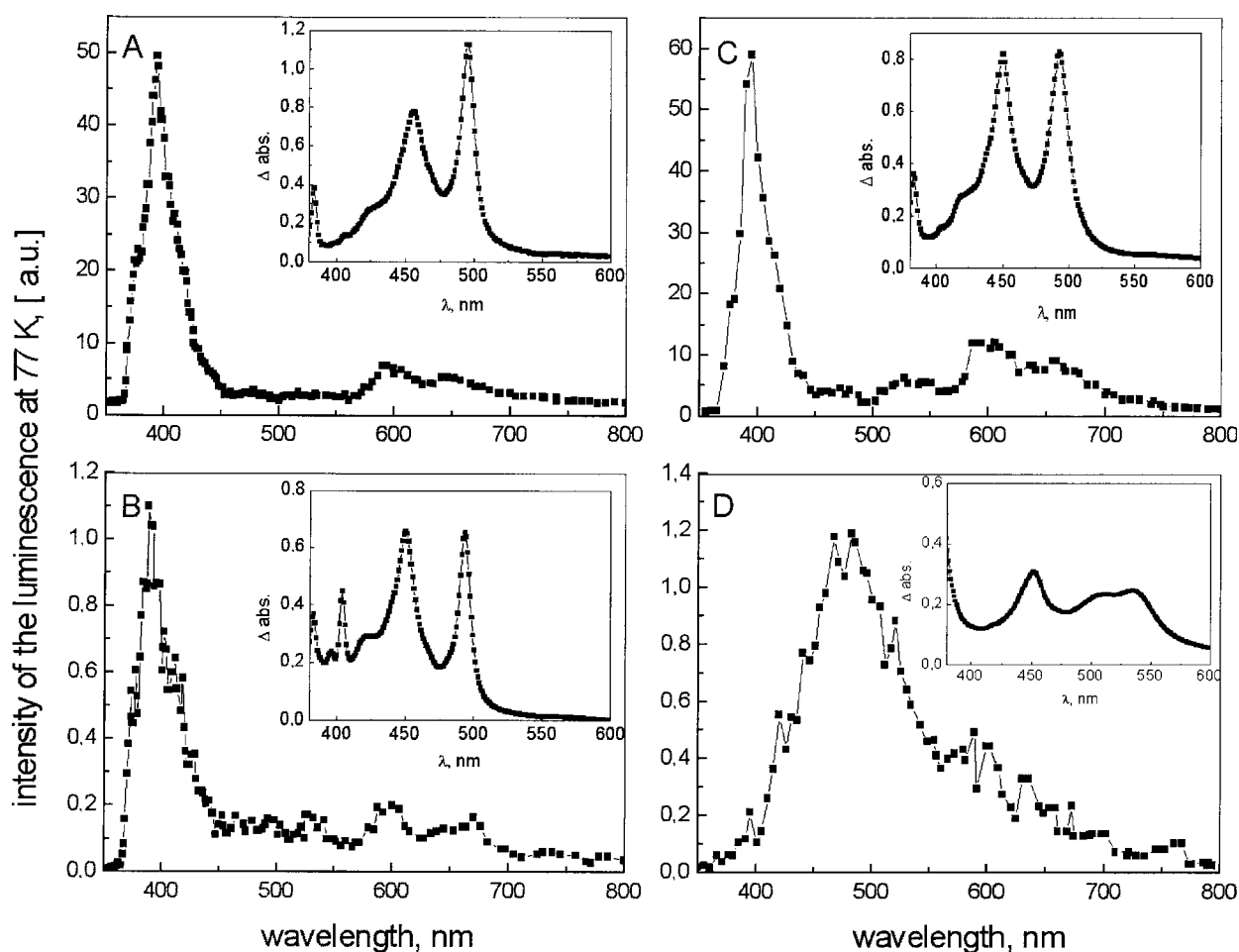


Fig. 1. Spectral distributions of the isothermal luminescence and absorption spectra (inserts) at 77 K of polymer-Py systems irradiated at 77 K with a dose of 4–6.5 kGy: (A): PE-Py ($\sim 10^{-2}$ mol·dm $^{-3}$); (B): PDMS-Py ($\sim 5 \times 10^{-3}$ mol·dm $^{-3}$); (C): PMMA-Py ($\sim 5 \times 10^{-2}$ mol·dm $^{-3}$); (D): PET-Py ($\sim 1.3 \times 10^{-1}$ mol·dm $^{-3}$). Adapted from: [15]-(A), [19]-(B), [16]-(C), [18]-(D).

the polymer glass transitions occurs [15, 19]. In PMMA-Py (Fig. 2C) and PET-Py (Fig. 2D) systems absorption bands assigned to negative ionic species disappeared completely in the examined temperature range, whereas the Py $^{*+}$ absorption bands were observed even in room temperature.

In the PMMA-Py system, a maximum of the wsRTL for 395 nm was observed at ~ 150 K, whereas that for 475 nm was shifted towards a higher temperature [16]. The transition temperatures known for PMMA are 150–170 K for the α -methyl group rotation (γ -relaxation) and 240–250 K for the ester group rotation (β -relaxation) [10]. One can conclude that such relaxation events can affect the charge recombination in PMMA.

The study of the spectral composition of radiothermoluminescence provides information both about the polymer matrix itself and about additives dissolved in it [26].

The spectral distributions of RTL for polymer-Py systems in the T_g region consisted of three emission bands assigned to Py singlet, excimer and triplet excited states. The contribution of these emission bands depended on the solute concentration and chemical structure of the polymer matrix [15, 17, 19]. Two emission bands: monomer and excimer fluorescence, and only traces of phosphorescence were observed in

the PE-Py system [15]. In PDMS-Py and PMMA-Py systems all three emission bands were recorded [17, 19]. The ratio of the excimer to monomer fluorescence intensities was higher for more Py concentrated systems [15, 17, 19]. One can suppose that for a higher solute concentration, the distance between Py molecules is shorter and the excimer configuration is favourable.

The Py phosphorescence generation can be explained taking into account the probability of formation of singlet or triplet states which should depend on the amount of energy released during recombination of charges. This energy depends on the depth of an electron stabilization trap. The deeper the trap for the electron (i.e. the higher EA of atoms or chromophore groups in the polymer chain), the smaller energy of recombination will be released and triplet excited state formation will be favourable.

The investigations of wsRTL of the PE-Py system [15] suggested the formation of additional anionic radical traps, $R^{\bullet-}$, that become mobile in the T_g region of PE. The neutralization of these species can be responsible for the traces of Py phosphorescence in the RTL spectrum recorded for the PE-Py system at T_g range.

In the PMMA-Py system, the contribution of phosphorescence band was dependent on the solute

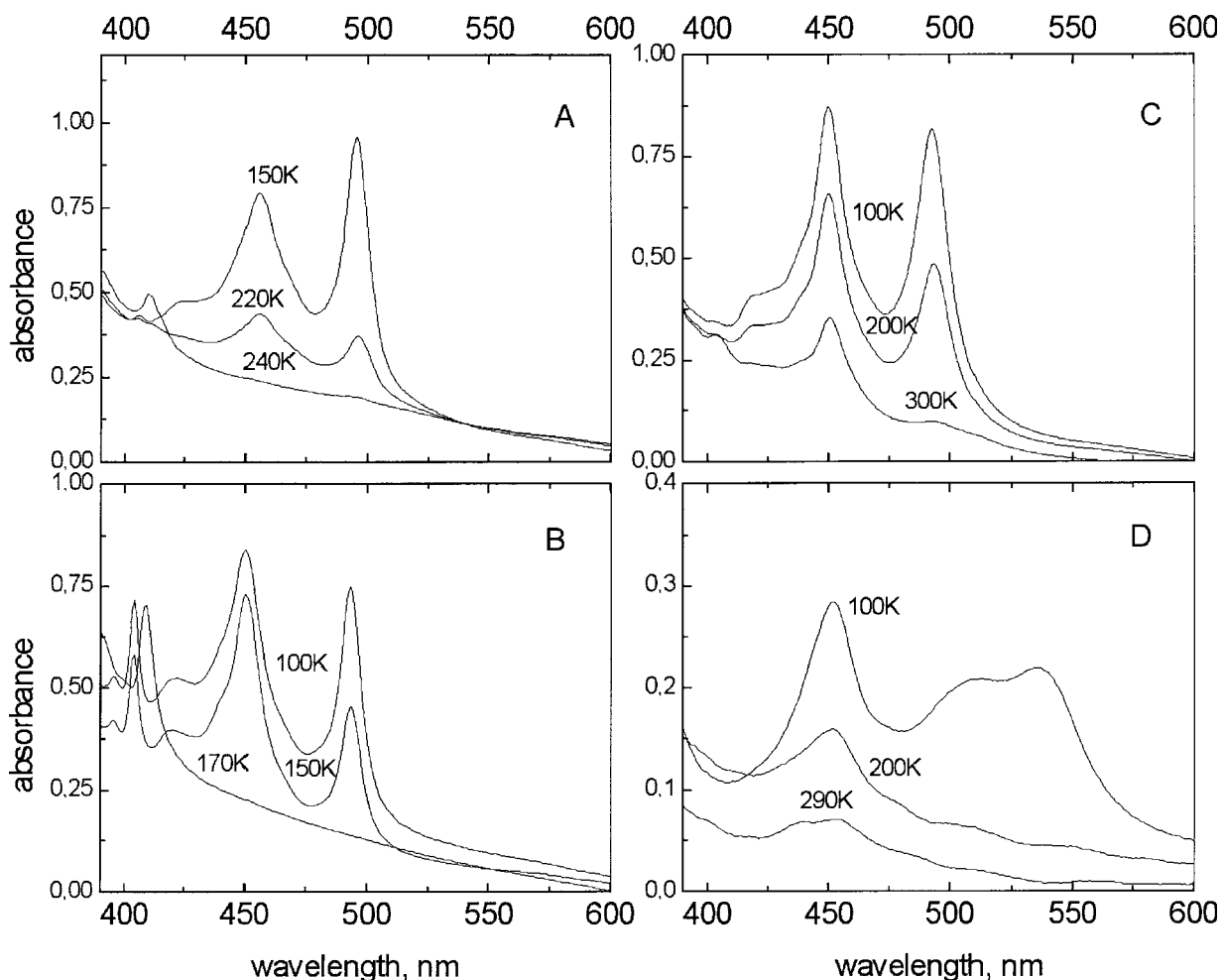


Fig. 2. The influence of temperature on the optical absorption spectra of (A): PE-Py ($\sim 10^{-2}$ mol·dm $^{-3}$), (B): PDMS-Py ($\sim 5 \times 10^{-3}$ mol·dm $^{-3}$), (C): PMMA-Py ($\sim 5 \times 10^{-2}$ mol·dm $^{-3}$) and (D): PET-Py (1.3×10^{-1} mol·dm $^{-3}$) systems irradiated at 77 K with a dose of 5–6.5 kGy. Adapted from [19]-(B), [16]-(C).

concentration. For Py concentration $\sim 10^{-2}$ mol·dm $^{-3}$ the RTL spectrum recorded at T_g range consisted of Py phosphorescence only [17]. This may be explained if one assumes that for low Py concentration not all electrons are scavenged by the solute and part of them reside in PMMA traps. Degradation of PMMA via main-chain scission reaction leads to the formation of low molecular weight radical ions $\text{CO}_2^{\cdot-}$ [9] that become mobile and recombine with $\text{Py}^{+\cdot}$ in the T_g range of PMMA giving the Py triplet states followed by Py phosphorescence.

The nature of electron traps in PDMS is unknown up to now [12]. Taking into account the presence of the phosphorescence band in the RTL spectrum recorded for the PDMS-Py system at 155 K [19] one can suppose that in this system the electrons are stabilized as matrix radical ions.

Conclusions

The efficiency of ionic neutralization in irradiated polymer systems depends on the solute concentration and on the polymer matrix properties (relaxation phenomena).

Long-lived separated ionic pairs: solute radical cations and polymer radical anions, can exist at room temperature in the polymers which can form the glassy state at room temperature ($T_g >$ room temperature; PMMA, PET).

Total neutralization of charges generated during irradiation of polymer systems occurs in the T_g range of the polymer matrix. The recombination of solute radical ions generates singlet excited states of the admixture followed by monomer and excimer fluorescence (depending on the solute concentration). The recombination of solute radical cations with polymer radical anions leads to the formation of solute triplet excited states followed by phosphorescence.

Acknowledgments The author is grateful to prof. J. Mayer (Institute of Applied Radiation Chemistry) for his helpful cooperation.

References

1. Beitz JV, Miller JR (1979) Exothermic rate restrictions on electron transfer in a rigid medium. *J Chem Phys* 71:4579–4595

- Boyer RF (1973) Glass temperatures of polyethylene. *Macromolecules* 6:288–299
- Brede O, Hermann R, Wojnarovits L, Stephan L, Taplick T (1989) Time-resolved characterization of radiation-generated species in molten polyethylene. *Radiat Phys Chem* 34:403–413
- Burger C, Kreuzer FH (1996) Polysiloxanes and polymers containing siloxane group, chapter 3. In: Kircheldorf HR (ed.) *Silicon in polymer synthesis*, Springer-Verlag, Berlin–Heidelberg, pp 113–222
- Hama Y, Kimura Y, Tsumura M, Omi N (1980) Studies on the recombination of cation-electron pairs by long-range tunnelling, as studied by ITL measurement in irradiated polymers. *Chem Phys* 53:115–122
- Ichikawa T, Yoshida H (1990) Mechanism of radiation induced degradation of poly(methyl methacrylate) as studied by ESR and electron spin echo methods. *J Polym Sci A* 28:1185–1196
- LaFemina JP, Arjavalingam G (1991) Photophysics of poly(ethylene terephthalate): ultraviolet absorption and emission. *J Phys Chem* 95:984–988
- Ogasawara M, Tanaka M, Yoshida H (1987) Reaction of solvated electron with poly(methyl methacrylate) and substituted poly(methyl methacrylate) in hexamethylphosphoramide studied by pulse radiolysis. *J Phys Chem* 91:937–941
- Sakai W, Tsuchida A, Yamamoto M, Yamauchi J (1995) Main chain scission reaction of poly(methyl methacrylate) caused by two-photon ionisation of dopant. *J Polym Sci A* 33:1969–1978
- Sommersall AC, Dan E, Guillet JE (1974) Photochemistry of ketone polymers. XI Phosphorescence as a probe of subgroup motion in polymers at low temperatures. *Macromolecules* 7:233–243
- Szadkowska-Nicze M (2002) Ionic processes in irradiated solid polymers. *Zeszyty Naukowe Politechniki Łódzkiej* 913:1–56 (in Polish)
- Szadkowska-Nicze M, Kulpiński J, Michalska ZM, Mayer J (1998) Pulse radiolysis study on transient species produced in polydimethylsiloxane. *J Photochem Photobiol A* 117:153–162
- Szadkowska-Nicze M, Mayer J (1998) Pulse radiolysis studies of poly(methyl methacrylate) containing pyrene. *J Polym Sci A* 36:1209–1215
- Szadkowska-Nicze M, Mayer J (1999) Investigation of transient species in pulse irradiated poly(ethylene terephthalate) film. *J Polym Sci A* 37:2853–2862
- Szadkowska-Nicze M, Mayer J (2000) Wavelength-selected radiothermoluminescence of polyethylene doped with pyrene. *J Polym Sci A* 38:3378–3382
- Szadkowska-Nicze M, Mayer J (2001) Ion recombination in PMMA doped with pyrene as observed by wavelength selected radiothermoluminescence. *Res Chem Intermed* 27:823–835
- Szadkowska-Nicze M, Mayer J (2002) Long-lived species generated via irradiation of poly(methyl methacrylate) containing pyrene. *J Polym Sci A* 39:4110–4118
- Szadkowska-Nicze M, Mayer J (2003) Ionic and excited species in irradiated poly(ethylene terephthalate) doped with pyrene. *J Photochem Photobiol A* 159:23–31
- Szadkowska-Nicze M, Mayer J (2004) Ionic and excited species in irradiated polydimethylsiloxane doped with pyrene. *J Polym Sci A* 42:6125–6133
- Szadkowska-Nicze M, Mayer J, Kroh J (1992) Pulse radiolysis of solid polyethylene in the presence of pyrene. *Radiat Phys Chem* 39:23–28
- Tagawa S, Hayashi N, Yoshida Y, Washio M, Tabata Y (1989) Pulse radiolysis on liquid alkanes and related polymers. *Radiat Phys Chem* 34:503–511
- Tanaka M, Yoshida H, Ogasawara M (1988) Formation and reaction of polymer ions in solutions studied by pulse radiolysis. *Radiat Phys Chem* 32:719–724
- Vrentas JS, Duda JL (1977) Diffusion in polymer-solvent systems. I. Re-examination of the free volume theory. *J Polym Sci B* 15:403–416
- Zhang G, Thomas JK (1996) Energy transfer via ionic processes in polymer films irradiated by 0.4 MeV electrons. *J Phys Chem* 100:11438–11455
- Zhang G, Thomas JK (1996) Radiation induced energy and charge transport in polystyrene laser photolysis and pulse radiolysis comparative study, chapter 3. In: Shalaby SW, Clough RL (eds) *Irradiation of polymers: fundamentals and technological applications*. ACS Symp Series, vol. 620. ACS, Washington, DC, pp 55–67 [and references therein]
- Zlatkevich L (1987) *Radiothermoluminescence and transitions in polymers* Springer-Verlag, New York