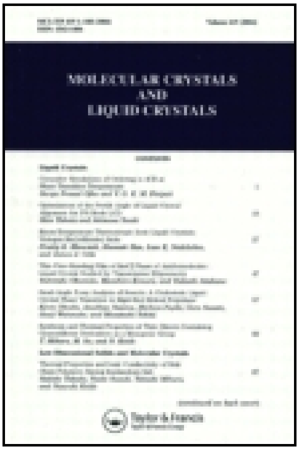

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Highly Mobile Charge Carriers in Poly(Di-n-Alkyl)Silanes in the Solid and in the Mesophase

Garrelt P. Van Der Laan [a] , Matthijs P. De Haas [a] , John M. Warman [a] , Holger Frey [b] & Martin Möuller [b]

[a] Radiation Chemistry Department, IRI, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands

[b] Chemical Technology, University of Twente, Postbus 217, 7500 AE, Enschede, The Netherlands

Version of record first published: 05 Dec 2006.

To cite this article: Garrelt P. Van Der Laan , Matthijs P. De Haas , John M. Warman , Holger Frey & Martin Möuller (1993): Highly Mobile Charge Carriers in Poly(Di-n-Alkyl)Silanes in the Solid and in the Mesophase, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 236:1, 165-172

To link to this article: http://dx.doi.org/10.1080/10587259308055224

Mol. Cryst. Liq. Cryst. 1993, Vol. 236, pp. 165–172
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

HIGHLY MOBILE CHARGE CARRIERS IN POLY(DI-*n*-ALKYL)SILANES IN THE SOLID AND IN THE MESOPHASE

GARRELT P. VAN DER LAAN*, MATTHIJS P. DE HAAS*, JOHN M. WARMAN*, HOLGER FREY+ and MARTIN MÖLLER+
* Radiation Chemistry Department, IRI, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands.
+ Chemical Technology, University of Twente, Postbus 217, 7500 AE, Enschede, The Netherlands.

Abstract Using the pulse-radiolysis TRMC technique the mobility and lifetime of radiation-induced charge carriers is studied in poly(di-*n*-alkyl)silanes with pentyl, hexyl and octyl sidechains in the solid and in the mesophase. A lower limit for the sum of the mobilities of the positive and negative charge carriers in the solid phase is estimated to be of the order of 10^{-5} $m^2V^{-1}s^{-1}$. The mobility is found to be dependent on the silicon backbone conformation. For the all-trans conformation the mobility is a factor of two larger than for the 7/3 helix conformation. At the I→II transition to the conformationally disordered mesophase the mobility drops an order of magnitude or more. The lifetime of the mobile charge carriers is found to increase with increasing sidechain length.

INTRODUCTION

Polysilanes attract wide attention because of their interesting electronic and optical properties[1,2]. A thorough understanding of the electronic properties is important before these materials can be used in promising applications in the fields of non linear optics[3] electrophotography[4], display fabrication[5] and data storage[6]. Although polysilanes are insulators in the pure state with band gaps of ca. 4 eV[7,8], photoconductivity with high quantum yields[9] and dark conductivity on doping[10] are observed.

Symmetrically *n*-alkyl substituted polysilanes display a transition (I→II) from a highly ordered low temperature phase (I)[11,12] to a partially disordered mesophase (II)[13]. Two silicon backbone conformations are known to exist in phase I dependent on the side chain length[1]. In the solid, low temperature phase of poly(di-*n*-butylsilane) and poly(di-*n*-pentylsilane), PDPS, the Si-backbone crystallizes in a 7/3 helix. In poly(di-*n*-alkyl)silanes with longer sidechains crystallization of the *n*-alkyl sidechains in phase I forces the silicon backbone into an all-trans planar zigzag conformation. At the I→II transition sidechain melting occurs which results in a liquid crystalline mesophase with a hexagonal columnar structure for all polymers. The columns consist of a disordered silicon chain in the centre surrounded by a molten hydrocarbon mantle. The optical and electronic properties of the polymers are predominantly determined by the structure of the silicon backbone. The role of the sidechains is indirect in tha they influence this backbone structure via intermolecular interactions.

We make use of the pulse-radiolysis time-resolved microwave conductivity (TRMC) technique[14-16] to study the mobility and decay kinetics of radiation-induced charge carriers on a timescale ranging from nanoseconds to milliseconds. Although we cannot determine the sign of the charge of the major carrier, the TRMC technique has a number of advantages over DC techniques. It is not necessary to make ohmic contact with the sample. Polarization effects caused by a constant applied electric field and grain boundary effects are absent. Because of this we are able to carry out experiments with powders and polymorphic materials Also the pulse-radiolysis TRMC technique provides a way of studying the mobility of the mobile charge carriers in these materials without the perturbations of the electronic and geometric structure caused by the presence of chemical dopants.

In an earlier study[17] we reported the abrupt change in the mobility and decay kinetics of radiation-induced charge carriers in poly(di-*n*-hexylsilane), PDHS, that was found to occur at the I→II transition. In this paper we describe the effects of sidechain length and silicon backbone conformation on the mobility and decay kinetics of radiation-induced charge carriers in the solid phase and in the mesophase of different polysilanes.

EXPERIMENTAL

Polymer synthesis

Symmetrically substituted di-*n*-alkyldichloro-silane monomers were prepared by Grignard reaction or via the hydrosilylation route. The high molecular weight polysilanes with *n*-pentyl, *n*-hexyl and *n*-octyl sidechains were synthesized by reductive coupling of the monomers with sodium in toluene/iso-octane as described elsewhere[18]. The molecular weights were determined by GPC referenced to narrow polystyrene standards. The polymers PDPS, PDHS and poly(di-*n*-octylsilane), PDOS, were found to have number average molecular weights of 2×10^5, 5×10^5 and 5×10^5 respectively. M_w/M_n ranged between 2 and 3, typical for the Wurtz-type coupling reaction[1].

Conductivity method

The polymers were compressed by hand into a piece of rectangular waveguide of cross-section 7.1×3.55 mm^2 closed at one end with a metal plate. The sample length was approximately 1 cm. Based on a density of 1 g/cm^3 for the bulk material, the fraction of bulk solid in the sample could be calculated from the measured weight and length.

The samples were ionized by irradiation with nanosecond pulses of 3 MeV electrons from a Van de Graaff accelerator. In this way a close to uniform distribution of mobile charge carriers is created throughout the sample. A typical 5 ns pulse of 4 A intensity deposits an energy per volume of 12 kJ/m^3, creating a concentration of charge carriers (electron-hole, (e^-–h^+) pairs) less than 6×10^{21} m^{-3} (10 μM).

Changes of the conductivity of a sample on irradiation were monitored as changes in the microwave power reflected by the sample. Because the measurements are made using a closed waveguide circuitry, broadband EMI noise induced by the excitation pulse is inherently filtered out. The TRMC technique is fully described elsewhere[14-16].

RESULTS AND DISCUSSION

Dose normalized radiation-induced conductivity transients were obtained for PDPS, PDHS and PDOS in phase I (Fig. 1) and in phase II (Fig. 2). The transients show in general disperse i.e. non-monoexponential decays. The timescale of the decay is much longer than the duration of the pulse. For clarity we will discuss the relevance of the end-of-pulse conductivity and the decay kinetics separately below.

End-of-pulse conductivity

The radiation induced conductivity change is related to the sum of the mobilities of the charge carriers (positive and negative), $\Sigma\mu$, and the concentration of the charge carriers present at time t, $N_p(t)$ by

$$\Delta\sigma(t) = e\,\Sigma\mu\, N_p(t) \tag{1}$$

In Eq. (1) e is the elementary charge. Under conditions of no charge recombination during the pulse, the concentration of charge carriers immediately following the pulse which deposits an energy per unit volume, D, (J/m^3) in the sample would be

$$N_p(0) = D\,/\,e\,E_p \tag{2}$$

In Eq. (2) E_p is the average electron-hole pair formation energy in eV for high energy radiation. Combining Eqs. (1) and (2) gives the relation between $\Sigma\mu$ and the conductivity at the end of the pulse, $\Delta\sigma_{eop}$

$$\Sigma\mu \geq E_p\,\Delta\sigma_{eop}/D = \Sigma\mu_{min} \tag{3}$$

The mobility calculated using (Eq. 3) is in effect the minimum value of the sum of the mobilities, $\Sigma\mu_{min}$, since it is assumed that all of the charge carriers that are initially formed contribute to $\Delta\sigma_{eop}/D$.

Energy deposition by electron radiation is proportional to the local electron density so that even for PDPS more than 85% of the energy is deposited initially in the saturated hydrocarbon mantles. From studies in alkanes it is known that in these materials only about 3 % of the initially formed e^--h^+ pairs escapes geminate recombination on a picosecond timescale[19]. However the silicon backbone would be expected to scavenge a large fraction of the electrons and holes formed within the hydrocarbon regions[20,21] prior to geminate recombination, since the interchain distance of ca. 15 Å[1] is much smaller than the average electron-hole pair separation distance of ca. 70 Å[22]. The conductivity transients observed on a nanosecond and longer timescale must therefore result from high, one-dimensional mobilities of electrons and/or holes along the silicon backbone.

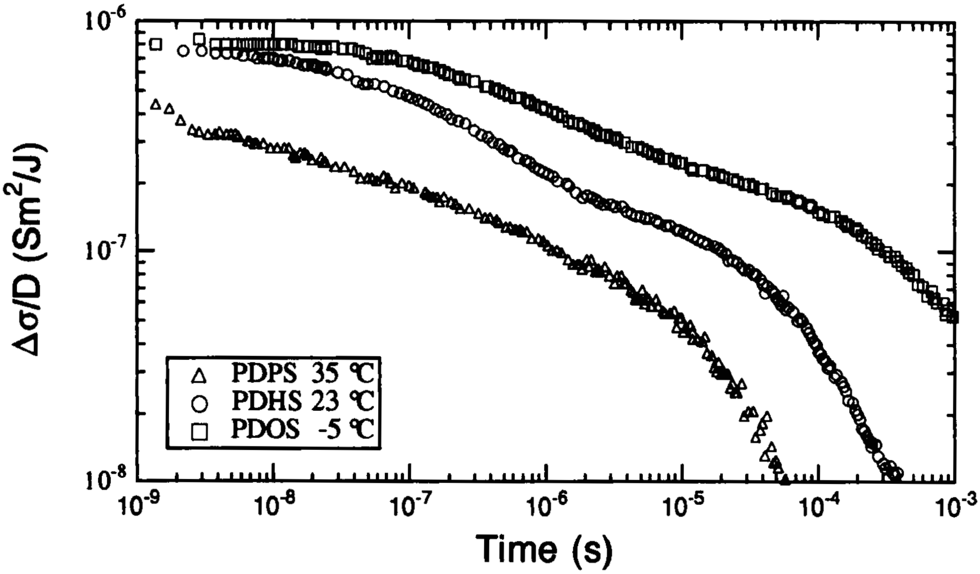

FIGURE 1 Dose normalized radiation-induced conductivity transients obtained in phase I at ca. 10 °C below the II→I transition. Use was made of 5 or 10 ns pulses depositing 10 to 25 kJ/m^3 per pulse.

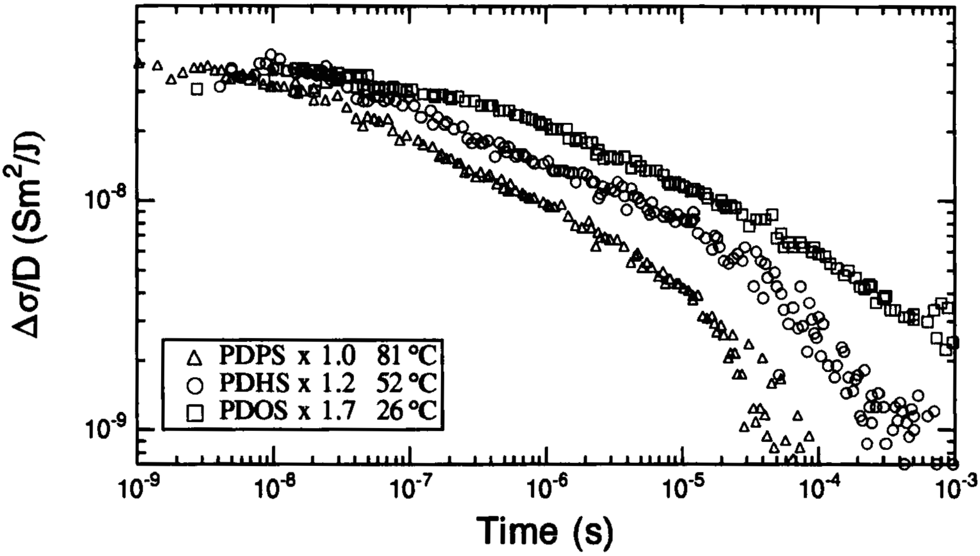

FIGURE 2 Dose normalized radiation-induced conductivity transients obtained in phase II at ca. 10 °C above the I→II transition. Use was made of 10 or 20 ns pulses depositing 25 to 45 kJ/m^3 per pulse. For better comparison of the transient kinetics the PDHS and PDOS transients were scaled to $\Delta\sigma_{eop}/D$ of PDPS by factors of 1.2 and 1.7 respectively.

It is apparent from Eq. (3) that if E_p is known, $\Sigma\mu_{min}$ can be determined. From studies of a large number of semiconductor materials, semi-empirical relationships linking E_p and the band gap, E_g, have been found. We use the relation given by Alig[23].

$$E_p = 2.73\ E_g + 0.5 \qquad (4)$$

Eq.(4) is found to give a reasonable estimate of E_p even for insulators such as saturated hydrocarbons. Taking the silicon backbone and the hydrocarbon sidechain regions to have their own values of E_g, ca. 4 eV[7,8] and ca. 8 eV[24] respectively, the electron density weighted average value of E_p changes only from 20.7 to 21.3 eV from PDPS to PDOS. Therefore we use the average value of 21 eV for the polymers studied both in phase I and phase II. The resulting values of $\Sigma\mu_{min}$ using Eq. (3) are listed in Table I.

TABLE I Pulse-irradiated polysilanes in phase I and II.

	Temp (°C)	phase	Si-backbone conformation	$\Delta\sigma_{eop}/D$ (10^{-8} Sm^{2}J^{-1})	$\Sigma\mu_{min}$ (10^{-7} m^{2}V^{-1}s^{-1})	$t_{1/2}$ (10^{-7} s)
PDPS	81	I	7/3-helix	37	78	1.3
	35	II	disordered	3.8	8.0	0.9
PDHS	23	I	all-trans	72	150	2.4
	52	II	disordered	3.1	6.5	3.0
PDOS	-5	I	all-trans	80	170	14.0
	26	II	disordered	2.2	4.6	20.0

The temperature dependences of $\Delta\sigma_{eop}/D$ for PDPS, PDHS and PDOS are shown in Fig 3. The transition temperatures found upon heating are 73, 42, and 11 °C for PDPS, PDHS and PDOS respectively. The transitions are identified as the I→II transition. The transition temperature and hysteresis upon cooling match the thermal behaviour found by DSC measurements and correspond to the literature values with the exception of PDOS for which a transition temperature of 47 °C has been reported[1].

$\Delta\sigma_{eop}/D$ decreases at the I→II transition by a factor 10, 23 and 36 for PDPS, PDHS and PDOS respectively. In Table I the $\Sigma\mu_{min}$ values are given for the different compounds at 10 °C above the I→II transition on heating and 10 °C below the II→I transition on cooling.

The decrease in $\Delta\sigma_{eop}/D$ at the I→II transition is attributed mainly to a change in the mobility of the charge carriers resulting from a change in backbone conformation. $\Sigma\mu_{min}$ seems to be determined by the conformation of the silicon backbone. The highest values of $\Sigma\mu_{min}$ of ca. 1.6×10^{-5} m^{2}V^{-1}s^{-1} are found in phase I of PDHS and PDOS (all-trans conformation). In phase I of PDPS (7/3 helix) $\Sigma\mu_{min}$ is a factor 2 lower. In phase II (disordered backbone) $\Sigma\mu_{min}$ is an order of magnitude or more lower than in phase I. Even in phase II the average value of $\Sigma\mu_{min}$ of 6×10^{-7} m^{2}V^{-1}s^{-1} is still high for a polymeric material.

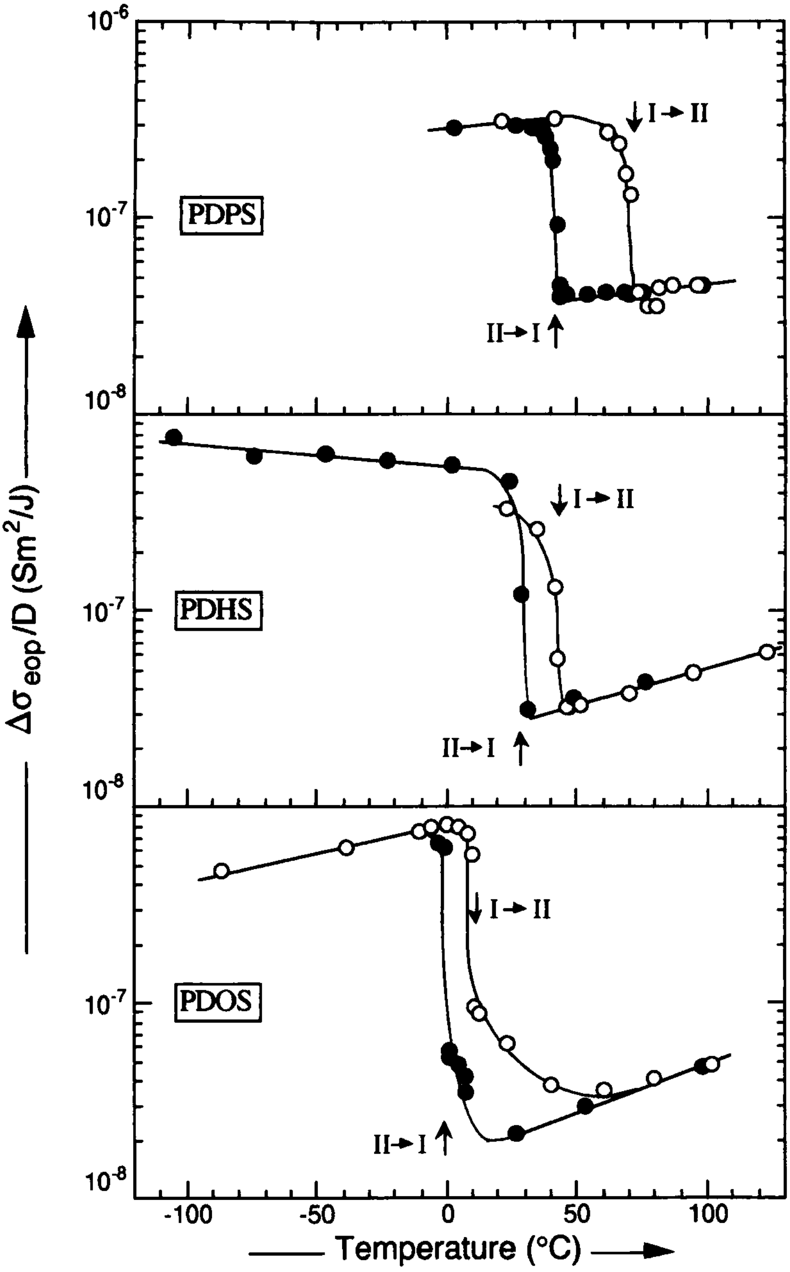

FIGURE 3 Temperature dependence of the radiation induced conductivity per unit dose, $\Delta\sigma_{eop}/D$, on heating (open circles) and on cooling (filled circles) in PDPS, PDHS and PDOS.

In time of flight (TOF) studies on PDHS[25] the major charge carrier, on a timescale of microseconds, has been determined to be the hole. The hole mobility is found to decrease at the I→II transition in qualitative agreement with the present study. However absolute values of the mobilities reported are 2-3 orders of magnitude smaller than our results.The lower values found by TOF measurements could be due to the longer timescale of the observations or to effects of microscopic inhomogeneites (domain boundaries, presence of amorphous regions) within the samples.

Decay kinetics

The observed radiation induced conductivity for all three polymers (Figs. 1 and 2) show disperse i.e. non-monoexponential decay kinetics. The decay of the conductivity can be due to recombination or to gradually deeper trapping of the charge carriers. The half lifetimes, $t_{1/2}$, found (Table I) increase with increasing the length of the sidechains. A similar effect of side chain length on the radiation induced conductivity has been found for octaalkoxy-phthalocyanines[26] and poly(*n*-alkyl)-thiophenes[27]. In the former study it was concluded that tunnelling of the charge carriers through the hydrocarbon layer determines the rate of charge recombination. We believe that a similar process is responsible for the decay of the conductivity in the polysilanes studied.

In phase I of both PDHS and PDOS there is an indication that the conductivity decay is bimodal. We propose as a possible explanation that the major charge carrier at the longest times is in all cases the hole, as indicated by TOF measurements[25], but that in the 'all-trans' solids electrons are also initially highly mobile but become localized, possibly in amorphous regions, within a few microseconds.

CONCLUSIONS

On pulsed irradiation long lived conductivity transients are found in the solid and in the mesophase of poly(di-*n*-alkyl)silanes. The mobility of the charge carriers is dependent on the conformation of the silicon backbone. A mobility of at least 10^{-5} $m^2V^{-1}s^{-1}$ is estimated for the charge transport along an all-trans silicon structure. The mobility is an order of magnitude or more lower for a disordered silicon chain which prevails in the liquid crystalline mesophase.

Longer sidechains have the effect of extending the lifetime of the mobile radiation-induced charge carriers.

ACKNOWLEDGEMENTS

The present investigation was supported by the Dutch Ministry of Economic Affairs Innovation-Oriented Research Programme on Polymer Composites and Special Polymers (IOP-PCBP).

REFERENCES

1 R.D. Miller and J. Michl, Chem. Rev., 89, 1359 (1989).

2 P. Trefonas III, R. West, R.D. Miller and D. Hofer, J. Polym. Sci., Polym. Lett. Ed., 21, 823 (1983).

3 F. Kajzar, J. Messier and C. Rosilio, J. Appl. Phys., 60, 3040 (1986).

4 K. Yokoyama and M. Yokoyama, Chem. Lett., 1005 (1989).

5 J. Kido, K. Nagai, Y. Okamoto and T. Skotheim, Chem. Lett., 1267 (1991).

6 M. Kakui, K. Yokoyama and M. Yokoyama, Chem. Lett., 867 (1991).

7 H. Tachibana, Y. Kawabata, S-Y Koshihara, T. Arima Y. Moritomo and Y. Tokura, Phys. Rev. B, 44, 5487 (1991).

8 K. Takeda, and K. Shiraishi, Phys Rev. B, 39, 11028 (1989).

9 M. Fujino, Chem. Phys. Lett., 136, 451 (1987).

10 R. West, L.D. David, P.I. Djurovich, K.L. Stearley, K.S.V. Srinivasan, Hyuk Yu, J. Am. Chem. Soc., 103, 7352 (1981).

11 F.C. Schilling, F.A. Bovey, A.J. Lovingerand J.M. Zeigler, in Silicon Based Polymer Science (Am. Chem. Soc., Washington D.C., 1990), pp 341-378.

12 H. Kuzmany, J.F. Rabolt, B.L. Farmer and R.D. Miller, J. Chem. Phys., 85, 7413 (1986).

13 P. Weber, D. Guillon, A. Skoulios and R.D. Miller, J. Physique France, 50, 793 (1989).

14 J.M. Warman and M.P. de Haas, in Pulse Radiolysis, edited by Y. Tabata (CRC press, 1990), Chap. 3, pp.101-133.

15 P.P. Infelta, M.P. de Haas and J.M. Warman, Radiat. Phys. Chem., 10, 353 (1977).

16 J.M. Warman, M.P. de Haas and H.M. Wentinck, Radiat. Phys. Chem., 34, 581 (1989).

17 H. Frey, M. Möller, M.P. de Haas, N.J.P. Zenden, P.G. Schouten, G.P. van der Laan and J.M. Warman, submitted for publication.

18 H. Frey, K. Matyjaszewski, M. Möller and D. Oelfin, Colloid Polym. Sci., 269, 442 (1991).

19 J.M. Warman, in The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis, edited by J.H. Baxendale and F. Busi (Reidel, Dordrecht, Holland, 1982), pp 433-533.

20 H. Ban, K. Sukagawa and S. Tagawa, Macromolecules, 20, 1775 (1987).

21 H. Bock, W. Kaim, M. Kira and R. West, J. Am. Chem. Soc., 101, 7667 (1979).

22 W.F. Schmidt and A.O. Allen, J. Phys. Chem., 72, 3730 (1968).

23 R.C. Alig, S. Bloom and C.W. Struck, Phys. Rev. B, 22, 5565 (1980).

24 J. Casanovas, R. Grob, D. Delacroix, J.P. Guelfucci and D.J. Blanc, J. Chem. Phys., 75, 4661 (1981).

25 M.A. Abkowitz, K.M. McGrane, F.E. Knier and M. Stolka, Mol. Cryst. Liq. Cryst., 183, 157 (1990).

26 J.M. Warman, M.P. de Haas, J.F. van der Pol and W. Drenth, Chem. Phys. Lett., 164, 581 (1989).

27 G.P. van der Laan, M.P. de Haas, A. Buik and B. de Ruiter, submitted for publication.