

Molecular Dynamics and Entropy Effects in Hydrogen-Bonded Supramolecular Polymer *N,N'*-Di(2-methyl-2-pentylheptyl)urea Dissolved in Nonpolar Medium

Jolanta Świergiel^{*,†}, Jan Jadżyn[†], and Laurent Bouteiller[‡]

Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, PL-60-179 Poznań, Poland, UPMC Université Paris 06, UMR 7610, Chimie des Polymères, F-75003 Paris, France, and CNRS, UMR 7610, Chimie des Polymères, F-75005 Paris, France

Received: September 21, 2009; Revised Manuscript Received: November 9, 2009

On the basis of the static dielectric permittivity temperature behavior of the supramolecular polymer formed by *N,N'*-di(2-methyl-2-pentylheptyl)urea (MPHU) in carbon tetrachloride diluted solution (10% in mole fraction) and that of neat acetonitrile, it was found that two liquids of the same macroscopic polarity (expressed by the same value of the dielectric permittivity ≈ 35) exhibit an essential difference in the field-induced orientational entropy change. A much higher entropy effect is observed for the liquid composed of not too numerous but highly polar molecular entities (MPHU + CCl₄) than for the liquid composed of numerous but less polar entities (neat acetonitrile). The analysis of the dielectric relaxation spectra of MPHU + CCl₄ solutions was performed with the Davidson–Cole (DC) model. It was found that the DC exponent β changes its value in a quite important range of 0.4–0.8, depending on MPHU concentration and temperature. This reflects an important deviation of the relaxation mechanism occurring in the supramolecular system investigated from that corresponding to the normal Brownian rotational diffusion ($\beta = 1$).

1. Introduction

Supramolecular polymers are formed in a spontaneous process of self-assembly of single molecules (monomers) through directional, noncovalent bonds created between them, mostly via hydrogen bonds.^{1–4} In comparison to the energy of covalent bonds in conventional polymers (typically 500 kJ/mol), the hydrogen bonds belong rather to weak interactions (typically 25 kJ/mol), so the supramolecular polymers can be relatively easily destroyed by the thermal energy. Such a type of reversible linkage between the basic elements of supramolecular polymers leads to their numerous unusual properties in comparison to those of conventional polymers.^{5–7} First of all, the reversible bonds allow one to control the basic property of the polymers—the mean degree of polymerization. It can be simply done by changing the temperature or concentration of a self-assembling compound dissolved in an appropriate solvent. So, one gains a possibility to engineer the multimolecular system of a given, well-defined physical property.

Many different molecular systems forming supramolecular polymers are presented in the literature,^{1–3} but among them *N,N'*-dialkylureas (R–NH•CO•NH–R) take a special place.^{8–15} Three active centers of the ureido group, –NH•CO•NH–, capable of forming the hydrogen bonds C=O•••H–N,¹⁶ are essential in the determination of the properties and activity of dialkylureas.^{17–19} The model of the dialkylurea multimers^{20,21} in which one molecule of urea is involved with four hydrogen bonds (Figure 1) (similar to the hydrogen-bonded water molecules) allowed one to explain an unusually strong increase of the molecular apparent dipole moment, observed with an increase of the concentration of dialkylurea in nonpolar medium. The proposed model has played an important role in understanding the exceptional ability to molecular self-association of a large family

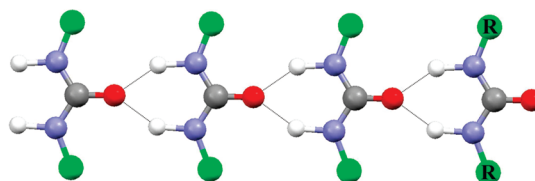


Figure 1. Model of a supramolecular polymer formed by *N,N'*-dialkylureas dissolved in nonpolar medium.

of urea-based supramolecular polymers and organogelators.^{22,23} In particular, the nonlinear optical properties of this class of compounds are of a special interest.^{24–28}

It is obvious that at a given temperature and concentration the degree of self-association of dialkylurea molecules depends mainly on the size of substituents R.²⁹ In the case of previously²⁰ studied compounds having the smallest possible substituents R (CH₃ or C₂H₅), the assembling process was so efficient that for the urea mole fraction of about 0.1% in carbon tetrachloride the supramolecular polymer chains contained several dozen molecules already.

However, in view of the liability of the interactions linking the molecular components together, the supramolecular chains have a dynamic character by nature. So, dielectric relaxation studies can provide here unique information on the molecular dynamics through watching the ways of equilibration of the dipolar system after its perturbation by an external electric field.^{30–32} The previous experiments have shown²⁰ that the dielectric relaxation spectra of highly self-organized systems (such as the solutions of dimethyl- or diethyl urea in nonpolar medium) exhibit the most simple form, i.e., the single Debye profile, indicating that the relaxation of the single mode is governed by an exponential pattern in the time domain. It is worth mentioning here that the dielectric relaxation spectrum of pure water, one of the most self-associated liquids, is also very close to the Debye form,^{33,34} similarly to many nonasso-

* Corresponding author. E-mail: swiergiel@ifmpan.poznan.pl.

[†] Polish Academy of Sciences.

[‡] UPMC Université Paris 06 and CNRS, Chimie des Polymères.

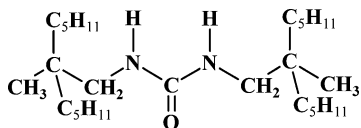


Figure 2. Chemical structure of *N,N'*-di(2-methyl-2-pentylheptyl)urea (MPHU).

ciated liquids.^{35,36} Hence, one might conclude that the dielectric relaxation processes recorded either in highly self-organized systems or in completely disordered polar liquids behave in a similar manner. Formally, in the two cases, the relaxation processes can be represented by a simple function of an exponential decay with time, characterizing the Markovian diffusion processes of Brownian character. Of course, between these two extreme liquids there are all kinds of intermediate, partially organized systems.

In this paper, we shall consider the static and dynamic dielectric properties of such an “intermediate” system of *N,N'*-dialkylurea with relatively large alkyl substituents: $-\text{CH}_2-\text{C}(\text{C}_4\text{H}_9)_2\text{CH}_3$, which quite efficiently reduce the extent of molecular self-association in nonpolar medium. The subject of the paper is an investigation of the self-association process, both in the static and in the dynamic regimes, as a function of the temperature and the concentration of that supramolecular polymer.

2. Experimental Section

The supramolecular polymer studied is *N,N'*-di(2-methyl-2-pentylheptyl)urea, MPHU (Figure 2), dissolved in the nonpolar medium (carbon tetrachloride). Synthesis and purification of MPHU were described previously.²⁹ Carbon tetrachloride of spectroscopic grade was purchased from Fluka. Measurements of the complex dielectric permittivity were performed in the frequency region of 50 kHz–100 MHz by using an HP 4194A impedance analyzer, and the measuring capacitor consisted of three plane electrodes: one central and two grounded on each side. The static values of the permittivity were taken as a low-frequency plateau of the real part of the complex dielectric permittivity. Due to an important electric conductivity of the samples with higher MPHU content, we analyzed the experimental dielectric data for MPHU + CCl_4 mixtures with the urea concentration up to about 10% (in mole fraction). The measurements were performed in the temperature range of 21–65 °C. The details of the experimental setup are described elsewhere.³⁷

3. Results and Discussion

In Figure 3 are presented, as an example, the dielectric relaxation spectra [dispersion $\epsilon'(\omega)$ and absorption $\epsilon''(\omega)$] recorded for MPHU + CCl_4 solution with urea mole fraction equal to 0.1, at different temperatures. Figure 4 presents the results in the complex plane ϵ'' vs ϵ' (the Cole–Cole plot) for two MPHU concentrations in carbon tetrachloride, at 65 °C. Two features of the spectra should be noted. First of all, as seen in Figure 3, a remarkable increase of the electric conductivity effect is observed when the temperature increases. Second, an asymmetric deviation of the Cole–Cole plots from the Debye’s semicircle form can be quite easily recognized in Figure 4. The main feature of that deviation, observed at the high-frequency side of the plots, is an acute angle between the tangent to the curve representing the experimental points and the real ϵ' axis, which leads to a skew effect in the Cole–Cole plot. The effect is observed in the whole MPHU concentration range and the temperature range studied. These experimental

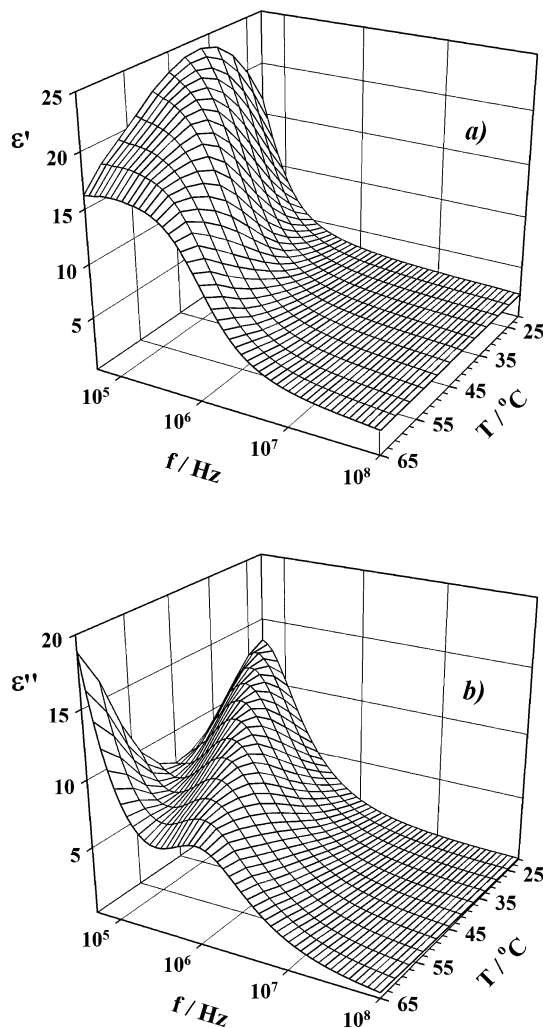


Figure 3. Dielectric relaxation spectra recorded for MPHU + CCl_4 solution of the urea mole fraction $x = 0.1$.

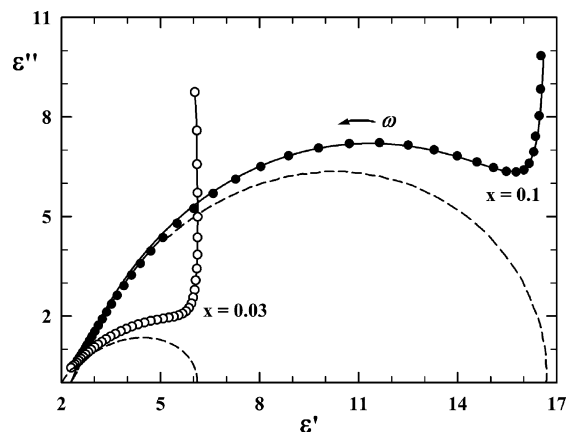


Figure 4. Cole–Cole plots for MPHU in CCl_4 solutions, at 65 °C. The solid lines represent the best fit of eq 1 to the experimental spectra. The dashed lines represent the Cole–Cole plots after withdrawing the electric conductivity effect. The fractional exponent β is equal to 0.54 and 0.75 for $x = 0.03$ and $x = 0.1$, respectively.

facts point out that here we are not dealing with a kind of superposition of some number of the dielectric absorption bands that, in principle, can give a similar spectroscopic effect as observed in our experiment. If this was the case, the intensities of the elementary bands would have to change exactly in the

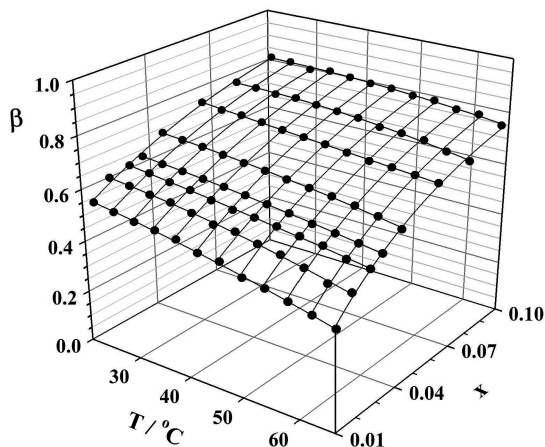


Figure 5. Temperature and concentration dependences of the fractional exponent β resulting from the best fit of the Davidson–Cole model ($\alpha \approx 1$, $0 < \beta < 1$) to the experimental dielectric spectra of MPHU dissolved in carbon tetrachloride. x denotes the urea mole fraction.

same way either as a function of the temperature or as a function of the concentration of self-assembling compound: this is unlikely.

Before a quantitative analysis of the dielectric relaxation spectra, we mention that the difference in the dielectric response of N,N' -diethylurea (DEU)²⁰ and studied MPHU is certainly due to a different ability to self-associate in nonpolar medium. As was recently shown by FTIR spectroscopy, the proportion of the shorter oligomers is significantly higher in MPHU solutions than in DEU ones.²⁹ In the case of DEU, the supramolecular chains are probably too long to relax as a whole, so they probably break apart into smaller chains to relax, whereas much shorter and polydisperse chains of MPHU can relax as whole entities.

The most general empirical expression, which is commonly used for the analysis of an experimental dielectric relaxation spectrum departing from the Debye form, was proposed by Havriliak–Negami^{38,39}

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{[1 + (i\omega\tau)^\alpha]^\beta} - i\frac{\sigma}{\varepsilon_0\omega} \quad (1)$$

where ω is the angular frequency of the probing electric field; τ is the relaxation time; ε_s and ε_∞ are, respectively, the static and high-frequency limits of the real part of the complex dielectric permittivity; σ is the electric conductivity; and $\varepsilon_0 = 8.85$ pF/m is the permittivity of free space. The fractional exponents α and β reflect the broadening of the dielectric absorption band, i.e., the deviation from the Lorentzian shape (Debye model). In particular, the case of $0 < \alpha < 1$ and $\beta = 1$ in eq 1 corresponds to the symmetrical broadening (the Cole–Cole equation⁴⁰), while for $\alpha = 1$ and $0 < \beta < 1$, one can analyze the asymmetric (skew) broadening (Davidson–Cole equation^{41,42}). For $\alpha = \beta = 1$, the well-known Debye equation is recovered.

The best fit of eq 1 to the dielectric relaxation spectra of MPHU + CCl_4 solutions yielded for the exponent α values very close to unity (0.98 ± 0.02), whatever the urea concentration and the temperature of solution. For the exponent β , on the contrary, one observes its rather strong dependence on both the urea concentration and the temperature, as shown in Figure 5. The temperature dependences of the two remaining fitting

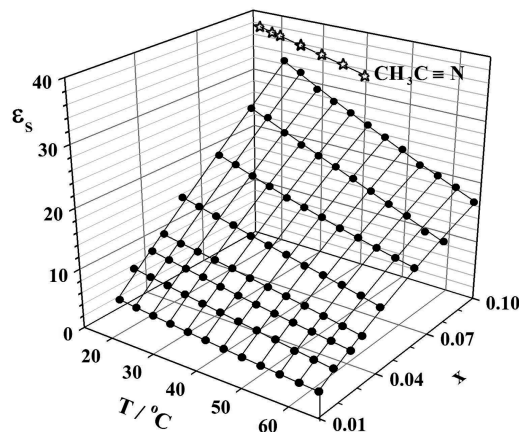


Figure 6. Temperature and concentration dependences of the static dielectric permittivity of MPHU in CCl_4 solutions. The permittivity data for acetonitrile are presented by \star .^{44–48}

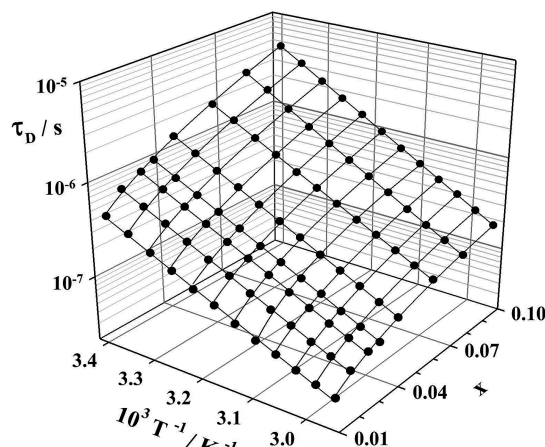


Figure 7. Temperature and concentration dependences of the dielectric relaxation time of MPHU dissolved in CCl_4 . At the constant urea mole fraction (x), the solid lines represent the best fit of the Arrhenius relation ($\ln \tau_D \propto E_A/T$) to the experimental data.

parameters, static dielectric permittivity (ε_s) and the dielectric relaxation time (τ_D), are depicted in Figures 6 and 7, respectively.

The anomaly recorded in the dielectric relaxation behavior of the supramolecular polymer studied here is of the Davidson–Cole type ($\alpha \approx 1$, $0 < \beta < 1$),^{41,42} and the behavior is similar to that observed for other N,N' -dialkylureas with a large alkyl substituent.⁴³ The dependences obtained for the fractional exponent β (Figure 5), representing the extent of the Davidson–Cole type anomaly in the dielectric relaxation spectra, clearly show that both with increasing the urea concentration (at constant temperature) and decreasing temperature (at constant concentration) the value of the exponent β increases. This indicates that with increasing degree of the molecular self-assembly the relaxation spectra become more and more close to the Debye pattern ($\beta = 1$).

The dielectric relaxation time of the supramolecular polymer studied is found in the 0.1–10 μs range, which reveals the existence of quite strongly developed association processes in the diluted solutions studied. As presented in Figure 7, the relaxation time exhibits an important dependence on MPHU concentration and temperature. The activation energy of the relaxation process, resulting from an Arrhenius dependence $\ln \tau_D \propto E_A/T$, is presented in Figure 8, as a function of MPHU mole fraction. A relatively high value of the activation energy and its important dependence on MPHU mole fraction, together

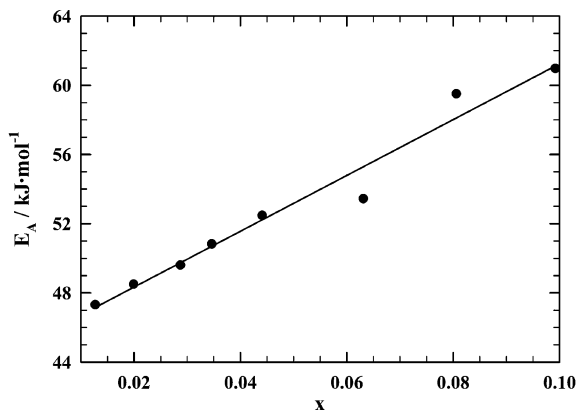


Figure 8. Arrhenius activation energy for the relaxation process as a function of the mole fraction x of MPHU in CCl_4 .

with the quite high value of the relaxation time, strongly support the conclusion that the highly polar supramolecular polymers formed in the solutions undergo the orientation and relaxation processes as whole entities.

Special attention should be paid to the temperature and concentration dependence of the static dielectric permittivity (ϵ_s) of MPHU + CCl_4 mixtures. As can be seen in Figure 6, the permittivity value strongly depends on MPHU concentration, and for the solution of 0.1 mol fraction, at 21 °C, $\epsilon_s \approx 35$. That value is quite close to the permittivity of some strongly polar pure liquids, such as acetonitrile, for example. The static dielectric permittivity values for neat acetonitrile are marked in Figure 6, at several temperatures.^{44–48} As can be clearly seen in the figure, the temperature variation of $\epsilon_s(T)$ for acetonitrile and MPHU + CCl_4 solution of $x = 0.1$, two liquids of very similar static permittivity values, are essentially different. This fact reflects the difference in the thermodynamic consequences of the orientational behavior of the entities formed in these two liquids. As was first shown by Fröhlich in 1958⁴⁹ and next by Becker,⁵⁰ Landau, Lifshitz, and Pitaevskii⁵¹ and Scaife,⁵² the temperature derivative of the static dielectric permittivity is directly related to the electric field induced increment of the entropy (ΔS) as follows

$$\frac{\Delta S}{E^2} \equiv \frac{S(T, E) - S_0(T)}{E^2} = \frac{\epsilon_0 \partial \epsilon_s}{2 \partial T} \quad (2)$$

where S_0 denotes the entropy of the liquid under investigation in the absence of the electric field; E is the amplitude of the probing electric field; and T is the absolute temperature. As it was shown in recent papers,^{53–56} the relation 2 allows one to perform precise studies on the orientational phenomena in strongly polar liquid crystalline materials. In these fluids, due to the molecular self-organization in the form of the antiparallel dipole–dipole arrangements in the pseudonematic domains, the probing electric field can induce in the isotropic liquid, in the vicinity of the transition to the nematic phase, even a positive change of the entropy ($\Delta S > 0$).

Figure 9 shows that in the whole MPHU concentration range studied the electric field, when applied to the solutions, causes a decrease of the entropy ($\Delta S < 0$); i.e., the field induces an ordering of the molecular dipoles in the system. The ordering effect, i.e., the negative value of ΔS , increases markedly with increasing concentration of the urea which reflects an increase of the degree of molecular self-association in the system, where gradually larger and larger linear multimers of high polarity

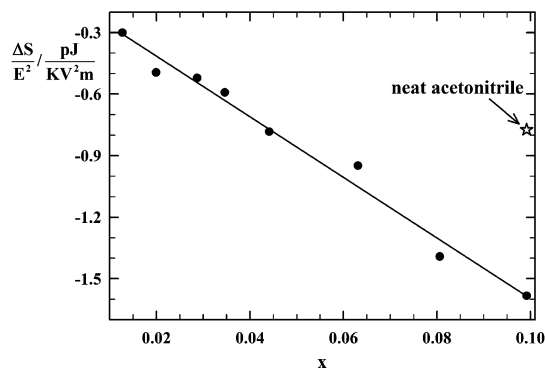


Figure 9. Entropy increment induced by the probing electric field in MPHU + CCl_4 solutions of different urea mole fraction x . The value for neat acetonitrile is given as ☆.

are created. For comparison, the magnitude of the entropy effect appearing in neat acetonitrile is also depicted in Figure 9, and hence, the following conclusion can be formulated. Two polar liquids of similar static permittivity values, when placed in an external electric field, give, from the entropy point of view, an essentially different response: the entropy increment induced by the field in neat acetonitrile consists of only half of the entropy effect observed in the diluted solution ($x = 0.1$) of the supramolecular compound in nonpolar medium. The difference must be a consequence of a different structure and composition of these two liquids. Namely, the neat acetonitrile is composed of a great number of rather small in size but quite strongly polar CH_3CN molecules (the molecular dipole moment is about $3.7 \pm 0.3 \text{ D}^{57,58}$). In contrast, the MPHU solution ($x = 0.1$) is composed in a great majority (90%) of nonpolar CCl_4 molecules, and only 10% are the urea molecules with a polarity (3.9 D^{20}) quite close to acetonitrile molecules. The macrodipoles formed by the self-assembled chains^{21,28,32,59} are certainly responsible for the more efficient electric field induced ordering, revealed by the larger entropy effect.

4. Conclusions

The results presented in the paper lead to the following more general conclusions. First, it results from the presented data that even in relatively diluted solutions the molecules are able to create the dielectric permittivity equivalent to that of a strongly polar neat liquid, provided the molecules in solution are capable of efficient self-organization via hydrogen bonds, forming linear and rigid supramolecular polymers of high polarity. Second, two liquids of the same macroscopic polarity (expressed by the same value of the dielectric permittivity) can show an essential difference in the field-induced orientational entropy change depending on the structure of the entities forming a given liquid. A much higher entropy effect can be expected for a liquid composed of few but highly polar molecular entities than for a liquid composed of numerous but less polar ones, even though the static dielectric permittivity of the two liquids has the same value.

Acknowledgment. The work was supported by MNiSzW grant number N N202 4123 33 (2008–2010).

References and Notes

- (1) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: New York, 1995.
- (2) Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D.; Vögtle, F.; Lehn, J.-M. *Comprehensive Supramolecular Chemistry*; Oxford: Pergamon, 1996.

- (3) Ciferri, A. *Supramolecular Polymers*, 2nd ed.; Taylor&Francis: Boca Raton, 2005.
- (4) Armstrong, G.; Buggy, M. *J. Mater. Sci.* **2005**, *40*, 547.
- (5) ten Cate, A. T.; Sijbesma, R. P. *Macromol. Rapid Commun.* **2002**, *23*, 1094.
- (6) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Ky Hirschberg, J. H. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601.
- (7) Cordier, P.; Tournilhac, F.; Soulie-Ziakovic, C.; Leibler, L. *Nature* **2008**, *451*, 977.
- (8) de Loos, M.; van Esch, J.; Kellogg, R. M.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 613.
- (9) Wang, G.; Hamilton, A. D. *Chem.—Eur. J.* **2002**, *8*, 1954.
- (10) Moreau, J. J. E.; Pichon, B. P.; Wong Chi Man, M.; Bied, C.; Pritzkow, H.; Bantignies, J.-L.; Dieudonné, P.; Sauvajol, J.-L. *Angew. Chem., Int. Ed.* **2004**, *43*, 203.
- (11) Vos, M. R. J.; Jardl, G. E.; Pallas, A. L.; Breurken, M.; van Asselen, O. L. J.; Bomans, P. H. H.; Leclere, P. E. L. G.; Frederik, P. M.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *J. Am. Chem. Soc.* **2005**, *127*, 16768.
- (12) Chebotareva, N.; Bomans, P. H. H.; Frederik, P. M.; Sommerdijk, N. A. J. M.; Sijbesma, R. P. *Chem. Commun.* **2005**, *39*, 4967.
- (13) Bouteiller, L.; Colombani, O.; Lortie, F.; Terech, P. *J. Am. Chem. Soc.* **2005**, *127*, 8893.
- (14) Vonau, F.; Suhr, D.; Aubel, D.; Bouteiller, L.; Reiter, G.; Simon, L. *Phys. Rev. Lett.* **2005**, *94*, 066103.
- (15) Colombani, O.; Bouteiller, L. *New J. Chem.* **2004**, *28*, 1373.
- (16) Gora, R. W.; Bartkowiak, W.; Roszak, S.; Leszczynski, J. *J. Chem. Phys.* **2002**, *117*, 1031.
- (17) Sucha, L. V.; Sathyanarayana, D. N. *J. Mol. Struct.* **1984**, *125*, 89.
- (18) Hadzi, D.; Kidric, J.; Knezevic, Z. V.; Barlic, B. *Spectrochim. Acta A* **1976**, *32*, 693.
- (19) Goodman, M.; Morehouse, F. *Organic Molecules in Action*; Gordon and Breach: New York, 1973.
- (20) Jadzyn, J.; Stockhausen, M.; Żywucki, B. *J. Phys. Chem.* **1987**, *91*, 754.
- (21) Masunov, A.; Dannenberg, J. J. *J. Phys. Chem. B* **2000**, *104*, 806.
- (22) Shikata, T.; Nishida, T.; Isare, B.; Linares, M.; Lazzaroni, R.; Bouteiller, L. *J. Phys. Chem. B* **2008**, *112*, 8459.
- (23) Bouteiller, L. *Adv. Polym. Sci.* **2007**, *207*, 79.
- (24) Idrissi, A.; Bartolini, P.; Ricci, M.; Righini, R. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4666.
- (25) Datta, A.; Pati, S. K. *J. Chem. Phys.* **2003**, *118*, 8420.
- (26) Datta, A.; Pati, S. K. *THEOCHEM* **2005**, *756*, 97.
- (27) Datta, A.; Pati, S. K. *Chem. Soc. Rev.* **2006**, *35*, 1305.
- (28) Pal, S.; Manna, A. K.; Pati, S. K. *J. Chem. Phys.* **2008**, *129*, 204301.
- (29) Lortie, F.; Boileau, S.; Bouteiller, L. *Chem.—Eur. J.* **2003**, *9*, 3008.
- (30) Wubbenhorst, M.; van Turnhout, J.; Folmer, B. J. B.; Sijbesma, R. P.; Meijer, E. W. *IEEE TDEI* **2001**, *8*, 365.
- (31) Shikata, T.; Kuruma, Y.; Sakamoto, A.; Hanabusa, K. *J. Phys. Chem. B* **2008**, *112*, 16393.
- (32) Sakamoto, A.; Ogata, D.; Shikata, T.; Urakawa, O.; Hanabusa, K. *Polymer* **2006**, *47*, 956.
- (33) Kaatz, U.; Uhlendorf, V. *Z. Phys. Chem.* **1981**, *126*, 151.
- (34) Barthel, J.; Bachhuber, K.; Buchner, R.; Hetzenauer, H. *Chem. Phys. Lett.* **1990**, *165*, 369.
- (35) Jordan, E. P.; Sheppard, R. J.; Szwarnowski, S. *J. Phys. D: Appl. Phys.* **1978**, *11*, 695.
- (36) Barthel, J.; Bachhuber, K.; Buchner, R.; Gill, B.; Kleebauer, M. *Chem. Phys. Lett.* **1990**, *167*, 62.
- (37) Jadzyn, J.; Bauman, D.; Déjardin, J.-L.; Ginovska, M.; Czechowski, G. *Acta Phys. Polon. A* **2005**, *108*, 479.
- (38) Havriliak, S.; Negami, S. *J. Polym. Sci. C* **1966**, *14*, 99.
- (39) Havriliak, S.; Negami, S. *Polymer* **1967**, *8*, 161.
- (40) Cole, K. S.; Cole, R. H. *J. Chem. Phys.* **1941**, *9*, 341.
- (41) Davidson, D. W.; Cole, R. H. *J. Chem. Phys.* **1950**, *18*, 1417.
- (42) Davidson, D. W.; Cole, R. H. *J. Chem. Phys.* **1951**, *19*, 1484.
- (43) Jadzyn, J.; Bouteiller, L.; Déjardin, J.-L.; Czechowski, G. *Acta Phys. Polon. A* **2006**, *110*, 495.
- (44) Kinart, C. M.; Kinart, W. J.; Kolasinski, A.; Ćwiklińska, A. *Phys. Liq. Chem.* **2000**, *38*, 583.
- (45) Kinart, C. M.; Kinart, W. J.; Ćwiklińska, A. *Phys. Liq. Chem.* **2001**, *39*, 589.
- (46) Kinart, C. M.; Kinart, W. J.; Ćwiklińska, A.; Chęcińska, D.; Dzikowski, T. *Phys. Liq. Chem.* **2003**, *41*, 197.
- (47) Kuila, D. K.; Lahiri, S. C. *Z. Phys. Chem.* **2004**, *218*, 803.
- (48) Helambe, S. N.; Lokhande, M. P.; Kumbharkhane, A. C.; Mehrotra, S. C.; Doraiswamy, S. *Pramana* **1995**, *44*, 405.
- (49) Fröhlich, H. *Theory of Dielectrics*, 2nd ed.; Clarendon Press: Oxford, 1958.
- (50) Becker, R. *Electromagnetic fields and interactions*; Blackie and Son: London, 1964.
- (51) Landau, L. D.; Lifshitz, E. M.; Pitaevskii, L. P. *Electrodynamics of continuous media*, 2nd ed.; Pergamon Press: Oxford, 1984.
- (52) Scaife, B. K. P. *Principles of Dielectrics*; Clarendon Press: Oxford, 1998.
- (53) Jadzyn, J.; Sokołowska, U.; Déjardin, J.-L. *J. Phys. Chem. B* **2008**, *112*, 9050.
- (54) Jadzyn, J.; Sokołowska, U.; Czechowski, G. *J. Phys. Chem. B* **2008**, *112*, 7022.
- (55) Jadzyn, J.; Czechowski, G.; Déjardin, J.-L. *J. Phys. Chem. B* **2008**, *112*, 4948.
- (56) Jadzyn, J.; Czechowski, G. *Opto-Electron. Rev.* **2008**, *16*, 395.
- (57) Breitung, E. M.; Vaughan, W. E.; McMahon, R. J. *Rev. Sci. Instrum.* **2000**, *71*, 224.
- (58) Grabuleda, X.; Jamie, C.; Kollman, P. A. *J. Comput. Chem.* **2000**, *21*, 901.
- (59) Datta, A.; Pati, S. K. *J. Phys. Chem. A* **2004**, *108*, 320.

JP909094X