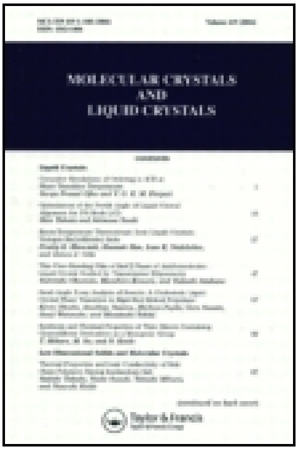

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Micelle Motion in Lyotropic Nematic Phases

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Micelle Motion in Lyotropic Nematic Phases

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Aqueous lyotropic liquid crystalline systems of Type I ($\Delta\chi > 0$), composed of finite cyclindrical micelles, and Type II ($\Delta\chi < 0$) composed of finite disc shaped micelles have been prepared in thermodynamic equilibrium with the parent mesophases "Hexagonal H_α" and "Lamellar L_α" respectively. The degree of order profile has been measured for all hydrocarbon segments by substitution of perdeuteriated amphiphiles in the mesophases and the determination of their deuterium quadrupole splittings. The related co-existent phases have degrees of order profile in the chains, which differ by a constant factor in each of the two cases. The order profile is lowered in the nematic liquid crystal because the micelles are finite in size and their symmetry axes can oscillate about the director of the mesophase. An upper limit for the oscillation angle has been estimated. For the case of Type II with finite bilayer disc micelles, the normal to the discs deviates a maximum of 27° from the director. For Type I with finite cylinders the maximum deviation of the cyclinder axes from the director is estimated as 23°. The approximations of these estimates are discussed as well as the viability of the nematic mesophases as models for bilayer and membrane model chemistry.

INTRODUCTION

A recent overview article[1] describes the status of research into aqueous lyotropic liquid crystals that align spontaneously in magnetic fields. There are two main classes, those with positive diamagnetic anisotropy, Type I ($\Delta\chi > 0$), and those with negative diamagnetic anisotropy, Type II ($\Delta\chi < 0$). The magnetic classification is more embracing than one liquid crystal form.[2,3] A recent study, submitted for publication,[3] shows that the classical "Hexagonal H_α" mesophase has Type I properties and the "Lamellar L_α" mesophase has Type II magnetic properties. These latter liquid crystals, which have repeating positional order of infinitely extending bilayers, can exist in equilibrium with mesophases that have orientational order of derived finite micelles, only.[3] The hexagonal H_α mesophase is composed of cylindrical infinite micelles disposed with axes parallel. The perpendicular plane to these axes have a two-dimensional hexagonal array of cylinder centres. At higher water contents the H_α phase may co-exist in equilibrium with a nematic-type mesophase composed of finite cylindrical micelles. This nematic-type liquid crystal displays the same Type I diamagnetic anisotropy as the H_α phase but has only orientational long-range order of the finite rod-like micelles.[3] A similar co-existence can occur between the Lamellar L_α multibilayer system, with one direction of repeating order perpendicular to the planes, and a nematic-type liquid crystal made up of disc-like bilayer micelles with long-range orientational order only. In the case of these latter phases, the magnetic behaviour is Type II. The nematic-type phases have been named Type I CM (cylindrical micelles) and Type II DM (disc micelles) mesophases.[3] The structure of one Type II DM mesophase has been determined in low-angle X-ray diffraction experiments.[4] This determined mesophase is composed of disc-micelles of bilayer thickness and greater than 1000 Å diameter, which are embedded in an aqueous bath of mean thickness 80–130 Å. The alignment of the nematic-type liquid crystals in magnetic fields is spontaneous, while that of the parent mesophases H_α and L_α, either occurs at a very slow rate or must be induced by heating and cooling cycles in the static magnetic field.[2,3]

The purpose of the present study is to compare the complete degree of order profile for the segments of an amphiphile in the mesophases with positional order H_α and L_α and the derived nematic Type I CM and Type II DM respectively. The H_α and Type I CM mesophases can be prepared in equilibrium at the same temperature[2,3,5] and so can L_α and Type II DM mesophases.[2,3] A comparison of degree of order in finite and infinite micelles of the same symmetry is an important test of their use as membrane models and leads to an estimation of the effect on degree of order of the motions of the body of the finite micelles compared to the infinite micelles from which they are derived.

The two-phase equilibrium systems chosen for study are those previously encountered.[2,3] A lamellar binary mesophase L_α of decylammonium chloride co-exists in equilibrium with a Type II DM nematic phase in a region of 53% by weight detergent. The Type I CM nematic phase formed by mixtures of potassium laurate, potassium chloride and water in weight 39, 2.6 and 58.4%, respectively, includes the co-existent H_α hexagonal mesophase in thermodynamic equilibrium. Temperatures appropriate for the co-existence of two mesophases are 26°C.

EXPERIMENTAL

Potassium laurate-d_{23} and decylammonium chloride-d_{21} were synthesized and purified as reported previously.[2,6,7] Proton NMR showed a deuteriation of 90% and 94% respectively. Mesophases were prepared with the following composition by weight: A. 38.95% KL-d_{23}, 2.58% KCl, 58.48% H_2O which contained 5% D_2O; B. 54.80% DACl-d_{21}, 45.20% H_2O which contained 5% D_2O, pH = 1 (HCl).

Deuterium magnetic resonance spectra were determined at 26°C on a Bruker SXP spectrometer operating at 9.2 MHz. Approximately 1,000–4,000 transients were required.

RESULTS

Cylindrical micelle/hexagonal system

It has been shown previously that the ternary system of KL/KCl/D_2O forms a hexagonal liquid crystalline system.[3] As the water content is increased, the quadrupole splitting for the D_2O decreases in a linear fashion until a phase change occurs (see Figure 1, Ref. 3). At this point there exists a small range of constant order parameter in which the hexagonal phase is in equilibrium with a second lyomesophase of lower quadrupole splitting. This mesophase has been shown to be Type I CM. Further dilution results in a single Type I CM mesophase whose order parameter again decreases with increasing water content, until an isotropic phase is achieved. It is the area of equilibrium between the hexagonal phase and the Type I CM lyomesophase which is of interest here. The Type I CM liquid crystal aligns in a few hours such that the director axis is parallel to the applied magnetic field. The observed quadrupole splittings are thus twice those which would be determined for a randomly oriented sample. The hexagonal phase in equilibrium with the CM system also aligns in the magnetic field, but much more slowly, alignment of approximately 50% of the sample being achieved over the course of one week.

The central portion of the ^2H NMR spectrum showing the HOD and terminal methyl resonances, after the sample had been placed in the magnetic field for 16 hours, is shown in Figure 1A. Note that while the CM mesophase has aligned during this time, very little alignment of the hexagonal phase has taken place. Figure 1B shows the same sample after approximately 100 hours. It is clear that the hexagonal mesophase is slowly aligning such that the director axis is parallel to the magnetic field, i.e. the "wings" of the powder pattern are growing at the expense of other orientations. The quadrupole splittings for the aligned Type I CM lyomesophase, the nonaligned hexagonal, and the aligned hexagonal mesophase are given in Table I. Also given in the table is the ratio of quadrupole splittings for all chain segments $\Delta\nu_i^{\mathrm{Type\,I\,CM}}/\Delta\nu_i^{\mathrm{Hexagonal}}$ for the individual positions along the chain, where $\Delta\nu_i^{\mathrm{Type\,I\,CM}}$ is the quadrupole splitting at position "i" of the Type I cylindrical micelle mesophase, and $\Delta\nu_i^{\mathrm{Hexagonal}}$ is the quadrupole splitting at position "i" of the

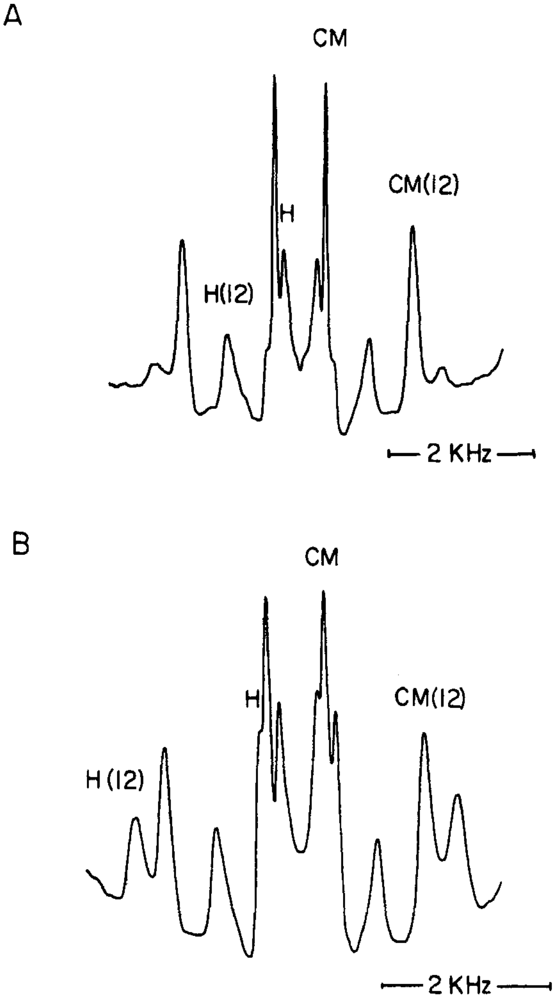

FIGURE 1 The central portion of the deuterium magnetic resonance spectrum of Type I cylindrical micelles in equilibrium with the hexagonal phase, showing the HOD and terminal methyl (position 12) resonances. A. After 16 hours in the magnetic field. The CM mesophase has aligned with its director parallel to the magnetic field, and is labelled on the right half of the symmetrical spectrum. The hexagonal phase shows very little alignment. The 90° quadrupole splittings are labelled on the left portion of the spectrum. B. After 100 hours in the magnetic field. Note the increased alignment of the hexagonal phase as indicated by the increased intensity of the 0° splitting. These are labelled on the left half of the spectrum. The scale of spectrum B is slightly expanded over that of spectrum A.

TABLE I

Quadrupole splittings[a] for co-existing type I cylindrical micelles and hexagonal lyomesophases.

	Quadrupole splitting (Hz)			
Position	CM	Hexagonal	Hexagonal (aligned)	$\frac{\Delta\nu^{\mathrm{Type\ I\ CM}}}{\Delta\nu^{\mathrm{Hexagonal}}}$
12	3143	1953	3906	0.80
11	9033	5682	11337	0.80
10	11444	7437	14874[b]	0.77
9	13672	9033[c]	18066[b]	0.76
8	15361	9766	19470	0.79
7	16357	10467	20752	0.79
3–6	18188	11832	22948	0.79
HOD	702	458	916	0.77

[a] Error is estimated to be less than 1 %.

[b] Calculated value from non-aligned resonance.

[c] Resonance co-incident with C11 of CM.

hexagonal mesophase. These ratios are constant at a value of 0.78 ± 0.02 for all chain segments, "*i*." Since these ratios are constant, it may be concluded that motion of the hydrocarbon chains of the trans/gauche type are identical in the two co-existing lyomesophases. Consequently, it may also be concluded that the interchain packing, and the anchoring of the head groups at the hydrophobic-hydrophilic interface which dictate the chain profiles, are the same in the Type I CM and hexagonal phases. Such a result lends credence to the proposal that the Type I systems are also composed of cylinders, but of finite length (3). Preliminary low-angle X-ray diffraction experiments are consistent with a cylinder diameter of 42 Å with no long-range positional order being detected.[8] The experimentally determined order parameter may be given by

$$S_{\mathrm{exp}} = S_{\mathrm{MO}} \cdot S_{\mathrm{CO}} \cdot S_{k/j} \cdot S_{\mathrm{diff}} \cdot \tfrac{1}{2}\langle 3\cos^2\Omega - 1\rangle \tag{1}$$

where S_{MO} is due to oscillation of the micelle as a whole about the director, S_{CO} is due to rigid body movement of the long axis of the chain in an oscillatory fashion about the perpendicular to the hydrophobic-hydrophilic interface, $S_{k/j}$ is due to segmental motion of the trans-gauche type which result in the formation of kinks and/or jogs in the chain long axis, S_{diff} is due to diffusion of amphiphiles around the edges of a finite micelle (edge effects), and Ω is the angle between the director of the lyomesophase and the applied magnetic field. In the case of Type I CM micelles and the aligned hexagonal phase, $\Omega = 0°$. Therefore Eq. 1 reduces to

$$S_{\mathrm{exp}} = S_{\mathrm{MO}} \cdot S_{\mathrm{CO}} \cdot S_{k/j} \cdot S_{\mathrm{diff}} \tag{2}$$

Since it is experimentally determined that motions of the kink/jog type are identical for the Type I CM and the co-existent hexagonal mesophases, it is reasonable that the rigid body chain oscillation about the perpendicular to the interface is also very similar. This is because factors affecting trans/gauche segmental motion, i.e. anchoring of the headgroup at the interface, and the tightness of amphipile-amphiphile packing also dictate the nature of chain oscillation. The constancy of the former for the two co-existent systems implies the invariance of the latter. Therefore we may write

$$\frac{S_{\text{exp}}^{\text{Type I CM}}}{S_{\text{exp}}^{\text{Hexagonal}}} = \frac{S_{\text{MO}}^{\text{Type I CM}}}{S_{\text{MO}}^{\text{Hexagonal}}} \cdot \frac{S_{\text{diff}}^{\text{Type I CM}}}{S_{\text{diff}}^{\text{Hexagonal}}} \tag{3}$$

where the superscripts Type I CM and Hexagonal refer to Type I cylindrical micelles and hexagonal lyomesophases, respectively. In the case of infinite cylinders, end effects are not possible and thus $S_{\text{diff}}^{\text{Hexagonal}}$ is identically equal to 1. As well, oscillation of the micelle as a whole about the director is not possible or of very small amplitude for infinitely long cylindrical micelles, and thus in this case, the angle between the director, and the magnetic field is constant at 0°. Therefore $S_{\text{MO}}^{\text{Hexagonal}} = 1$, and Eq. 3 reduces to

$$\frac{S_{\text{exp}}^{\text{Type I CM}}}{S_{\text{exp}}^{\text{Hexagonal}}} = S_{\text{MO}}^{\text{Type I CM}} \cdot S_{\text{diff}}^{\text{Type I CM}} \tag{4}$$

This ratio, as stated previously has been experimentally determined to be 0.78 (see Table I). Thus there exist rigid body motions possible for finite length cylinders which are not possible for cylinders of infinite length. As shown in Eq. 4, there exists two possibilities for the cause of the lowering of the ratio from a value of 1.00 to a value of 0.78. The first of these is the oscillation of the finite micelle as a whole, while the second is diffusion around the ends of the micelle. Simple geometrical considerations reveal that "end effects" are expected to be very small (less than 2% for a cylinder as short as 500 Å in length). Thus it is the oscillation of the micelle as a whole which results in the uniform lowering of the quadrupole splittings of Type I CM lyomesophase vs. those for the hexagonal phase. Since the experimentally determined order parameters are proportional to the observed deuterium quadrupole splittings

$$\frac{\Delta\nu^{\text{Type I CM}}}{\Delta\nu^{\text{Hexagonal}}} = S_{\text{MO}}^{\text{Type I CM}} = 0.78 \tag{5}$$

and

$$S_{\text{MO}}^{\text{Type I CM}} = \tfrac{1}{2}\langle 3\cos^2\theta - 1\rangle \tag{6}$$

where θ is the average angle between the director and the applied magnetic field. Thus θ is a measure of the micelle oscillation. Solving Eqs. 5 and 6 for θ

yields an average oscillation of the director about the magnetic field of 23° for the Type I cylindrical micelles. This angle is a maximum upper limit because $S_{\text{diff}}^{\text{Type I CM}}$ and $S_{\text{MO}}^{\text{Hexagonal}}$ may suffer small deviations from unity.

Disc/lamellar system

Decylammonium chloride/water binary mixtures form lyomesophases which are known to be of lammellar form.[2,9,10] However, with increasing water content it has been shown that this lamellar mesophase co-exists with a Type II DM lyomesophase of lower order parameter over a range of approximately 1% change in water content. This region of co-existence is at high water content, with further dilution resulting in an isotropic phase.[2] The Type II disc micelles align in a few minutes when placed in an applied magnetic field with the director axis (the bilayer normal) perpendicular to the applied magnetic field (i.e. Ω in Eq. (1) = 90°). The co-existent lamellar system may also be aligned by heating to an isotropic phase, and allowing the sample to cool in the magnetic field. The lamellar mesophase of larger quadrupole splitting becomes almost completely aligned by this cycle such that the director is perpendicular to the applied magnetic field. Assignments were made by comparison of spectra in which either the DM system alone, or both the co-existent DM and lamellar systems were aligned, and by comparison with previous studies of decylammonium chloride lyomesophases which employed specifically deuteriated detergent molecules.[11] The deuterium magnetic resonance spectrum of the two aligned co-existent mesophases is shown in Figure 2, while the quadrupole splittings for all the resonances

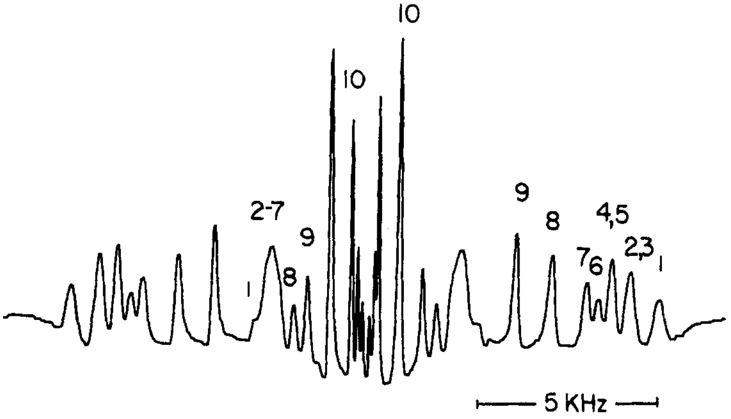

FIGURE 2 Deuterium magnetic resonance spectrum of a binary mixture of decylammonium chloride/water in which Type II disc micelles are in equilibrium with the lamellar phase. The disc micelle peaks are labelled on the left side of the symmetrical spectrum, while the resonances of the lamellar mesophase are assigned on the right.

TABLE II

Quadrupole splittings[a] for co-existing Type II disc micelles and lamellar lyomesophases.

Position	Quadrupole Splitting (Hz) Disc micelle	Lamellar	$\frac{\Delta\nu^{\text{Type II DM}}}{\Delta\nu^{\text{Lamellar}}}$
10	748	1907	0.39
9	3204	8362	0.38
8	3968	10376	0.38
7		12390	
6	5371	13001	
4,5		13733	0.39[b]
2,3		14648	
1	6165	16327	0.37
HOD	183	458	0.40

[a] Error is estimated to be less than 1 %.

[b] Represents positions 2–7 DM/a weighted average of positions 2–7 lamellar.

of the detergent chain are given in Table II. Also given in the table is the ratios of the quadrupole splittings $\Delta\nu_i^{\text{Type II DM}}/\Delta\nu_i^{\text{Lamellar}}$ for all positions "i" on the deuteriated chains. As in the case of the Type I/hexagonal co-existence region, these ratios are also constant, at a value of 0.39 ± 0.02. Since these ratios are constant, it may once more be concluded that trans/gauche type motions are the same for these two co-existing lyomesophases. Therefore a similar structure for the mesophases is indicated, which is in agreement with the finite disc-shaped micelles indicated by low-angle X-ray diffraction. Once again the absolute values of the quadrupole splittings for the DM mesophase are lowered by a constant amount compared with the classical infinite lamellar liquid crystal. In other words, micelle motions not possible for infinite lamellae are responsible. "End effects" are deemed to be larger than for the Type I DM system, but not appreciable (<8 %). As in the case of the CM/hexagonal system we may write

$$\frac{S_{\text{exp}}^{\text{Type II DM}}}{S_{\text{exp}}^{\text{Lamellar}}} = \frac{S_{\text{MO}}^{\text{Type II DM}}}{S_{\text{MO}}^{\text{Lamellar}}} \cdot \frac{S_{\text{diff}}^{\text{Type II DM}}}{S_{\text{diff}}^{\text{Lamellar}}} \tag{7}$$

where the superscripts Type II DM and Lamellar refer to the Type II disc micelle and lamellar lyomesophases respectively. Assuming the end effects are not important, and a constant angle of 90° between the director of the lamellar mesophase and the applied magnetic field yields.

$$\frac{\Delta\nu^{\text{Type II DM}}}{\Delta\nu^{\text{Lamellar}}} = \frac{\frac{1}{2}\langle 3\cos^2\theta - 1\rangle}{\frac{1}{2}\langle 3\cos^2 90^\circ - 1\rangle} = 0.39 \tag{8}$$

Solving for θ gives a value of 63° for the Type II DM lyomesophase as opposed to 90° for the lamellar system. Thus angular deviations of the director due to average micelle oscillations of 27° are calculated.

DISCUSSION

It has been shown that oscillations of the finite micelles of Type I CM and Type II DM of 23 and 27° respectively, account for the constant lowering of deuterium quadrupole splittings over those observed for the classical lyomesophases with which they are in equilibrium. It is interesting to note that the angle for the Type II DM system is larger than for the Type I CM system. Part of this difference may be due to small edge effects, i.e. diffusion of amphiphiles around the ends of the micelles. As stated previously, the edge effects, although small, are most probably larger in the case of the disc micelles. Larger edge effects would lead to a smaller ratio for $\Delta\nu^{\mathrm{Type\ II\ DM}}/\Delta\nu^{\mathrm{Lamellar}}$ and thus a larger calculated angle of oscillation.

The magnitudes of the angles of micelle motion are plausible, taking into account the fact that they represent upper limits. Small wave-like oscillations of the director in the hexagonal and/or lamellar systems would lead to too large an angle being calculated for the additional motion of the finite micelles. If the finite micelles possessed positional order (in actual fact they do not), using a bilayer thickness of ~40 Å, and an average intermicelle distance of 100 Å,[4] together with a micelle diameter of 1000 Å, it is possible to calculate a lower limit for Type II DM micelle oscillation of 14°. This assumes totally rigid micelle units, with no cooperativity in their movement, as well as positional order which is not present with these systems. In view of this the experimentally determined values for micelle motion reasonably describe the actual state of the system.

It is extremely interesting that motions of the trans/gauche type are the same for the two components of both the Type I CM/hexagonal system and the Type II DM/lamellar system. Since the effective length of a hydrocarbon chain is a function of the number and average position of gauche rotations[12,13] it follows that the cylinder thickness of the co-existent Type I CM and hexagonal mesophases are identical as is the bilayer thickness of the equilibrium mixture of the Type II DM and lamellar systems.

CONCLUSION

The ternary hexagonal potassium laurate/electrolyte/water lyomesophase may exist in equilibrium with a lyomesophase of Type I which is made up of finite cylindrical micelles (CM). The Type I system which has no long-range positional order of the micelle units aligns in an applied magnetic field such that the director axis is parallel to the magnetic field. The hexagonal phase is also Type I ($\chi > 0$) and nucleates from the CM phase with which it is in equilibrium by gaining two-positional degrees of order, i.e. CM liquid crystals are an intermediate state between the classical hexagonal phase, and the isotropic phase. The structure of the CM and hexagonal phases are very similar as shown by a constant ratio for the observed quadrupole splittings $\Delta\nu^{\text{Type I CM}}/\Delta\nu^{\text{Hexagonal}} = 0.78$ for individual amphiphile chain segments. The lower values for the experimentally determined order parameters of the CM lyomesophase may be accounted for by an oscillation of the finite cylinders, with a maximum deviation of the alignment of their axes of approximately 23° from the magnetic field (also director in this case).

Similarly, the binary lamellar decylammonium chloride/water lyomesophase may exist in equilibrium with a lyomesophase of Type II which is made up of finite disc-like micelles (DM). The Type II system, again which possesses no long-range positional order of the micelle units, aligns in an applied magnetic field such that the director axis is perpendicular to the field. The lamellar phase is also Type II and is aligned by heating until isotropic and allowed to cool in the magnetic field. The structures of the DM and the co-existent lamellar phases are very similar as shown by a constant ratio for the observed quadrupole splittings $\Delta\nu^{\text{Type II DM}}/\Delta\nu^{\text{Lamellar}} = 0.39$. This result in in agreement with low-angle X-ray diffraction results for other Type II lyomesophases.[4] The lower values for the experimentally determined order parameters of the DM mesophase in a constant ratio for all chain segments are accounted for by oscillation of the normal to the finite discs through an average angle of 27° from the director of the mesophase.

Similar studies are now in progress using electron spin resonance of specifically nitroxide substituted amphiphiles.

Acknowledgements

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