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ARTICLE TYPE

Individual photoreorientation of non-aggregated and aggregated azobenzene side chains tethering to a liquid-crystalline polymer determined by higher order derivative spectra

Kunihiro Ichimura[*a] **and Shusaku Nagano**[b]

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Higher order derivative spectra were applied to UV-VIS spectral changes of a liquid-crystalline polymer with azobenzene side chains exposed to linearly polarised 436 nm light at an elevated temperature to reveal the participation of non-aggregated as well as two types of aggregated species in in-plane as well as out-of-plane photoreorientation individually.

The photo-induced dichroism of polymer films referred to as the Weigert effect[1] has been attracting ever increasing interest owing to the breakthrough[2,3] leading to the photomodulation of refractive indices,[2c,2d] the surface-mediated liquid crystal (LC) photoalignment,[2f,3] photoorientation of molecular nanostructures[3d, 4] and so on.[2c,4] This sort of photodichroism (PD) has been attained by exposure to linearly polarised light (LPL) or oblique irradiation even with non-polarised light (NPL).[5] The optical anisotropy stems from the polarised photochemistry including photodimerisation and/or photoisomerisation. In particular, the photoreorientation of azobenzene units attached to LC polymer chains has been played a significant role in this research area because of the enhancement of PD due to liquid crystallinity. Polarised electronic absorption spectra have been basically employed to follow and evaluate PD by determining changes in absorbance with use of monitoring LPL of electric vector perpendicular to (A_s) as well as in parallel with (A_p) that of actinic light. A_s and A_p at λ_{max} have been used to specify PD because of the fact that λ_{max} is an elementary parameter for the characterisation and identification of molecules. Note here that an electronic absorption band consists of many sub-bands of a chromophore and its aggregate(s) circumstantially so that PD values at λ_{max} do not always reflect the well-defined electronic transition of photoreactive moieties. This work deals with tracing the generation of PD of an LC polymer with azobenzene side chains by means of derivative spectra to disclose photoreorientation behaviour of non-aggregated and aggregated azobenzenes individually. This is the first example for applying higher order derivative spectra to analyse polarisation photochemistry of polymer films, to the authours' knowledge.

Our previous studies on films of pAz-1 and the related LC polymers with different spacer lengths were performed systematically to disclose the in-plane (parallel) as well as the out-of-plane (perpendicular) photoreorientation upon LPL irradiation at 436 nm[6] as well as at 365 nm.[7] The out-of-plane photoreorientation upon exposure to NPL at 436 nm was also investigated.[8] But no information was available at that time concerning the role of aggregation in photoreorientation. Meanwhile, we reported recently that higher order derivative spectra of photosensitive polymers provide novel information about the identification and the role of aggregated species of photodimerisable side chains in photocrosslinking.[9,10] Fourth order derivatives have been employed predominantly previously because of the suitable separation of weak sub-peaks. In the case of water-soluble poly(vinyl alcohols) with styrylpyridinium (SbQ) side chains in anomalously low contents, derivative spectra reveal the presence of H-aggregate, which photodimerises quite rapidly when compared with isolated counterpart.[9] It was disclosed also by derivative spectra of hyper-branched polycinnamates that even cinnamate side chains form J-aggregate to undergo rapid photodimerisation.[10] The results motivated us to examine PD of pAz-1 upon exposure to LPL at 436 nm by means of higher order derivatives.

The absorption spectra of a solution and a spin-cast film of pAz-1 and a solution of the corresponding monomer (mAz-1) were taken on a diode-array spectrometer (Agilent 8453) with spacing between wavelength points of 1 nm. Absorbances of all samples at λ_{max} were normalised, and the absorption spectra are shown in Fig. 2a. The substantial broadening of the π,π^*-band is induced in film, while the absorption spectra of pAz-1 and mAz-1 are practically identical to confirm the absence of aggregation in polymer solution. The normalised absorption spectra were converted into second, fourth and sixth order derivatives, which were subjected to the spectral smoothing according to Savizky-Golay algorism under optimised conditions as described in our

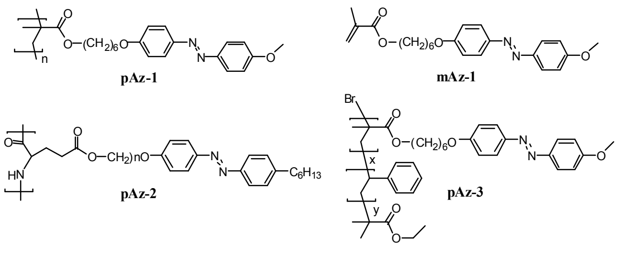

Fig. 1 The structure of azo-polymers and the monomer

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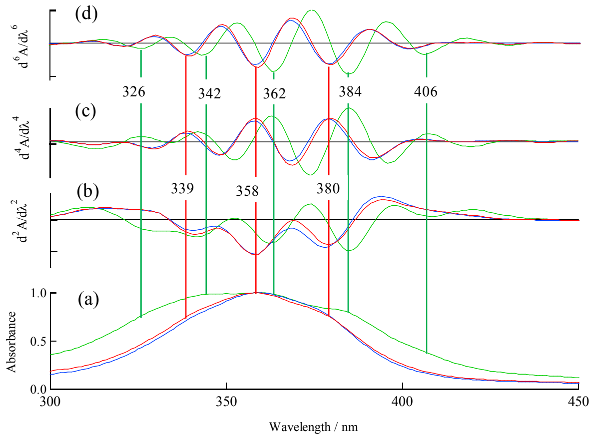

Fig. 2 (a) Normalised absorption and (b) the corresponding second, (c) fourth and (d) sixth order derivative spectra of pAz-1 in solution a 5.61x 10^{-6} mol/L solution (red lines) and film (green lines) and of mAz-1 in a 3.19 x 10^{-5} mol/L solution (blue lines). The numerical numbers correspond to the wavelengths of sub-peak positions in the fourth derivative.

previous reports[9,10] to give the spectra compiled in Figs. 2b, 2c and 3d, respectively.[9,10] Note that extrema in the second and sixth derivatives appear at the minima while those in the fourth order derivative at maxima.[11] The wavelengths of peak positions in the fourth derivatives of solution and film are put in Fig. 2. The shapes of absorption spectra of pAz-1 and mAz-1 are essentially identical in dilute solutions, and three sub-peaks are centred at the same wavelengths at 339 nm, 358 nm and 380 nm in dilute solutions of pAz-1 and mAz-1. The fact confirms that no intra-macromolecular aggregation is formed in a polymer solution. Consequently, it is reasonable to assume that the fine-structured π,π*-band consists of sub-peaks assignable to vibration level transition (VLT) of non-aggregated species just as in the cases of SbQ[9] and cinnamate[10] as linear-conjugated chromophores, since they are separated at the same distance of 1600 ± 30 cm^{-1} within measurement errors. Whereas the sub-peaks are red-shifted in film and appear at 342 nm, 362 nm and 384 nm, respectively, they are separated at the same distances of 1600 ± 20 cm^{-1} in line with the assignment to VLT of non-aggregated azobenzene.

Two new sub-peaks are detectable at 326 nm and 406 nm in the derivative spectra of a pAz-1 film, resulting in the marked broadening of the absorption band. The energy gap between 326 nm and 342 nm of one of the VLT peaks is 1430 cm^{-1} and distinctly smaller than that of VLT of the π,π*-band so that the 326 nm peak stems from H-aggregate with plane-to-plane stacking.[12] The other peak at 406 nm exists at a distance of 1410 cm^{-1} from the longest sub-peak of non-aggregated species at 384 nm. The possibility to regard this one as a satellite of the fourth derivative is reasonably eliminated, since an inflection appears at the corresponding wavelength in the second-order derivative. Thus, the 406 nm peak is plausibly assigned to J-aggregate in end-to-end stacking,[12] leading to the broadening of analytical band to the longer wavelength region. Therefore, the azobenzene in film exists in non-aggregated, H-aggregated and J-aggregated states. Notice here that the extremum value of the n-th order derivative is proportional to $(1/W)^n$ for an analytical band with a full width at half maximum *W*, which seems to be different among sub-peaks.[11] Since *W* of VLT bands is obviously smaller than that of absorption bands of aggregates stemming from electronic level transitions, the peak height of the former is much larger that of the latters, as seen in Fig. 2.

The assignment of aggregates of azobenzene side chains was previously performed on the basic of curve-fitting procedure.[13,14] Menzel et al. fitted the π,π*-band of a model compound of polyglutamates with *p*-hexylazobenzene side chains (pAz-2) in solution to a single Gaussian to achieve the curve-fitting. The curve-fitting of pAz-2 in LB films and even in solution was carried out by adding two peaks, which were claimed to be due to H- and J-aggregates, respectively.[13] The same approach was used by Zhao et al. to separate three bands due to H-aggregate, non-aggregate and J-aggregate of diblock copolymers (pAz-3) derived from mAz-1.[14] The bands in film were reported to be centred at 334 nm, 360 nm and 384 nm, respectively, whereas the wavelengths of H- and J-aggregates are distinctly different from our results, even though the azobenzene chromophore is quite the same. Such discrepancy between the present work and the previous report[14] should come from the fact that the fine structure of the π,π*-band due to VLT is thoroughly neglected in the curve-fitting approach. Accordingly, the discussion based on the distribution of non-aggregate and the aggregates estimated by the curve-fitting method is needed to be reconsidered.

pAz-1 exhibits the mesophase changes denoted as G 76 S 95 N 137 I. Photoirradiation of pAz-1 films with 436 nm light was conducted at 85°C to give *trans*-rich photostationary state in order to maintain smectic phase and to enhance the thermal *cis*-to-*trans* reversion to eliminate the contamination with *cis*-isomer as a minor component in absorption spectra. Fig 3a shows spectral changes during the course of irradiation with NLP irradiation. The band due to π,π*-transition declines rapidly to reach to a photostationary state at exposure doses of less than *ca* 80 mJ cm^{-2}. No substantial alteration occurred for the benzenoid band at *ca*. 250 nm. As revealed previously,[8] the reduction of π,π*-band arises from the out-of-plane reorientation to minimise

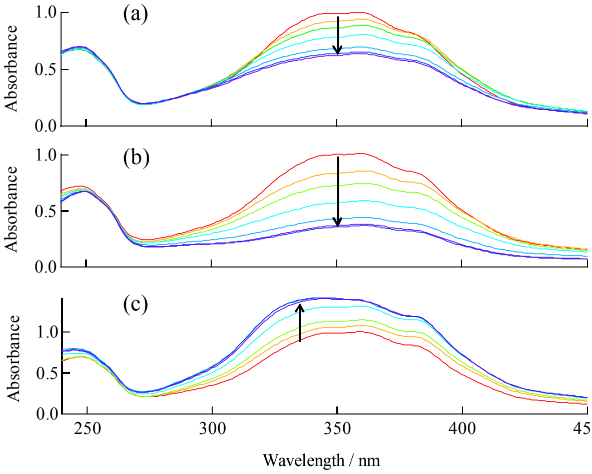

Fig. 3 Changes in absorption spectra of a pAz-1 film (a) upon exposure to NPL at 436 nm and in absorption spectra of pAz-1 films exposed to LPL at 436 nm and monitored with LPL with electric vector (b) in parallel with and (c) perpendicular to that of the actinic light, respectively.

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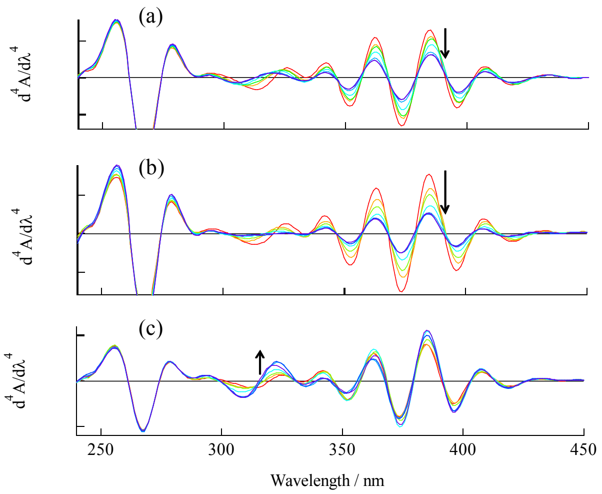

Fig. 4 Changes in the fourth order derivative spectra of pAz-1 films upon exposure to NLP at 436 nm light (a) and those in the fourth-order derivative spectra of pAz-1 films exposed to LPL at 436 nm and monitored with LPL with electric vector (b) in parallel with and (c) perpendicular to that of the actinic light, respectively.

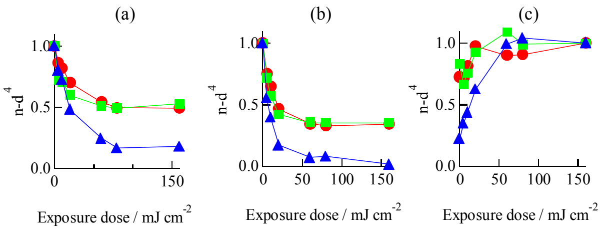

Fig. 5 Changes in normalised d^4 values of non-aggregate (circles) at 385 nm, J-aggregate (squares) at 406 nm and H-aggregate (triangles) at 326 nm or 324 nm as a function of exposure energy of (a) NPL at 436 nm and LPL at 436 nm when monitored with LPL of electric vector (b) in parallel with and (c) perpendicular to that of the actinic LPL.

light absorption by moving the transition moment toward the direction in parallel with the propagation direction of actinic light.[5] Fig. 3b shows changes in polarised absorption spectra monitored by LPL of electric vector in parallel with that of the actinic light. The absorption band declined owing to the out-of-plane reorientation. The in-plane reorientation is selectively monitored by LPL of the electric vector perpendicular to that of the actinic light, giving the marked enhancement of the analytical band, as shown in Fig. 3c.

All of the results are in line with our previous discussion,[6-8] whereas no information is available from absorption spectra with respect to the individual reorientation processes of non-aggregated and aggregated species. Subsequently, the spectral changes illustrated in Fig. 3 were converted into those of fourth order derivatives, which are compiled in Fig. 4. As seen in Fig. 4a, NPL irradiation led to the monotonous reduction of extrema of non-aggregated azobenzene at 342 nm, 362 nm and 384 nm and J-aggregated species at 406 nm, respectively. On the other hand, the reduction of sub-peak at 326 nm due to H-aggregate is accompanied by blue shift to 323 nm at the early stage. Note that the Beer's law is maintained in derivative spectra also.[11] Accordingly, changes in derivatives of a single process exhibit common crossing points throughout the spectra just as in the case of absorption spectra displaying isosbestic point(s). The present system is apparently free from *cis*-isomer, as pointed out above, so that the process contains solely the alteration of molecular axis of *trans*-isomer from random to uniaxial orientation. Consequently, the fact that no common crossing point is generated at least in the wavelength region shorter than *ca*. 340 nm confirms that the NPL irradiation results not only in the out-of-plane reorientation of H-aggregate, but also changes in aggregation mode. The existence of common crossing points at the wavelength region longer than *ca*. 340 nm suggests that the reorientation of non-aggregated as well as J-aggregate species occurs as single processes, respectively. In short, NPL irradiation leads to the out-of-plane reorientation of non-aggregated and J-aggregated species independently, while the out-of-plane reorientation of H-aggregate is accompanied by the modification of aggregation mode. Changes in the derivatives under LPL irradiation resemble those for NPL irradiation, as shown in Fig. 4b, whereas sub-peaks are reduced markedly because of the involvement of the in-plane reorientation. The polarised fourth order derivatives presented in Fig. 4c demonstrate changes arising from the in-plane reorientation in a way different from those shown in Figs. 4a and 4b. The sub-peak due to H-aggregate hiked noticeably after the shift of λ_{max} from 326 nm to 323 nm at the early stage.

In order to monitor changes in sub-peak height, d^4 values were normalised as shown below, whereas n-d^4, d_i^4 and $d_f^{\,4}$ are normalised d^4 and d^4 values before and after prolonged photoirradiation, respectively. For non-aggregate and J-aggregate species exhibiting the decrease in d^4, n-d^4 is equal to d_f^4/d_i^4, while n-$d^4 = d_i^4/d_f^4$ for H-aggregate displaying the increment of d^4. Fig. 5 shows the changes in n-d^4 of the three species as a function of exposure doses. The sub-peaks at 385 nm, 406 nm and 326 nm or 324 nm were chosen for the three kinds of species. As seen in Fig. 5a, the decrement of non-aggregated and J-aggregated species under NPL irradiation proceeds at an identical speed to reach to the final n-d^4 of 0.50. In contrast, n-d^4 of H-aggregate at 326 nm is levelled off at 0.18 and far smaller than those of the other two. This is because NPL irradiation leads not only to the out-of-plane reorientation, but also to blue shift of peak position at the early stage, as stated above. Figs. 5b and 5c correspond to the individual reorientation of the three species upon LPL irradiation. Fig. 5b reveals that their final n-d^4 is smaller than those under NPL irradiation because of the additional consequence of the in-plane reorientation. The in-plane reorientation of each species is specifically presented in Fig. 5c. n-d^4 values of H-aggregate are employed at 323 nm here and saturated at an exposure dose of 80 mJ cm^{-2}. The increment of n-d^4 for non-aggregated and J-aggregated species occurs moderately though fairly scattered possibly because of instrumental errors. Anyway, the considerable boost of changes in n-d^4 of H-aggregate suggests that non-aggregated species as well as J-aggregate reorient in the in-plane manner.

The growth of PD of individual species was successfully monitored by means of fourth order derivatives. Fig. 6a shows the emergence of PD expressed as $\Delta A = A_p - A_s$ as a function of wavelengths upon exposure to LPL. The dominant growth of ΔA

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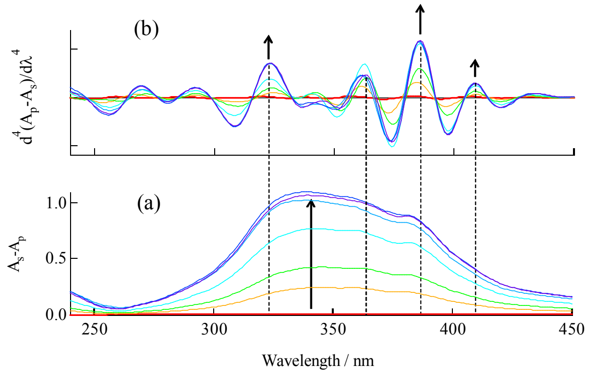

Fig. 6 (a) The generation of PD (A_s-A_p) of a pAz-1 film and (b) the changes in the corresponding fourth order derivatives as a function of exposure energy of LPL at 436 nm.

is observed in the wavelength region of H-aggregate, whereas the shorter wavelength region due to the benzenoid absorption with less anisotropy is quite low. Changes in the derivative spectra shown in Fig. 6b disclose that it is possible to discuss the induction process of PD of non-aggregated and aggregated species separately. Normalised values of d^4 at 326 nm, 385 nm and 406 nm, respectively, were plotted against exposure doses of LPL, and the results are summarised in Fig. 7. Because of a smaller change of d^4 at 406 nm relative to those at 326 nm and 385 nm, care should be taken in comparing a speed of dichroic generation of J-aggregate with those of non-aggregated and H-aggregated species. On account of comparable heights of sub-peaks at 326 nm and 385 nm, it is reasonable to claim that the dichroic generation of H-aggregate takes place slower than that of non-aggregated species. Such a delay may be interpreted in terms of the successive occurrence of the in-plane reorientation of non-aggregated azobenzene side chains, followed by the H-aggregation.

In conclusion, fourth order derivatives of a pAz-1 film enabled us to identify non-aggregated, H-aggregated and J-aggregate species of azobenzene side chains and to follow their LPL-induced dichroic generation individually. The NPL irradiation leads to the out-of-plane reorientation of non-aggregated and J-aggregated species, while H-aggregate suffers from the alteration of the aggregation mode at the early stage. Upon exposure to LPL, H-aggregate with transition moment in parallel with the polarisation plane of the actinic light suffers from the sufficient out-of-plane reorientation and the in-plane reorientation accompanied by the alteration of aggregation mode at the early stage. The generation of PD due to H-aggregate delayed measurably when compared with non-aggregated species probably because the H-aggregation of non-aggregated species occurs after the in-plane reorientation. The present approach with aid of higher order derivatives plays a novel role in revealing the generation of PD of the other types of photosensitive polymers.

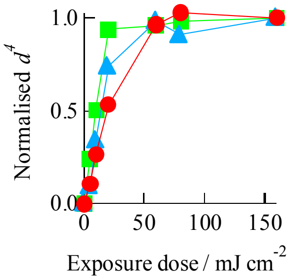

Fig. 7 Normalised d^4 values at 323 nm (red circles), 385 nm (green squares) and 406 nm (blue triangles) as a function of exposure dose.

Notes and references

[a] *R & D centre, Murakami Co. Ltd., 1-6-12 Ohnodai, Midori-ku, Chiba 267-0056, Japan. E-mail: k_ichimura@murakami.co.jp*
[b] *Nagoya University, Venture Business Laboratory, Furo-cho, Chikusa, Nagoya 464-8603, Japan. E-mail: snagano@apchem.nagoya-u.ac.jp*

1. F. Weigert, Naturewissenschaften, 1921, **29**, 583
2. a) T. Todorov, L. Nikolova, N. Tomova, *Appl. Opt.*, 1984, **23**, 4309; b) M. Eich, J. H. Wendorff, B. Reck, H. Ringsdorf, *Makromol. Chem. Rapid Commun.*, 1987, **8**, 59; c) J. Stumpe, L. Műller, D. Kreisig, G. Hauck, H. D. Koswig, R. Ruhmann, J. Rübner, *Makromol. Chem., Rapid Commun.* 1991, **12**, 81; d) R. Hagen and T. Bieringer, *Adv. Mater.*, 2001, **13**, 1805; e) V. A. Barachevsky, *J. Photopolym. Sci. Technol.*, 1991, **4**, 177; f) Z. Sekkat and W. Knoll eds. *Photoreactive Organic Thin Films*, Academic Press, 2002; g) V. G. Chigrinov, V. M. Kozenkov, H. -S. Kwok, *Photoalignment of Liquid Crystalline Materials: Physics and Applications*, John Wiley & Sons Ltd, West Sussex, 2008.
3. a) K. Ichimura, *Chem. Rev.* 2000, **100**, 1847; b) M. O'Neill and S. M. Kelly, *J. Phys. D Appl. Phys.*, 2000, **33**, R67; c) O. Yaroshchk and Y. Reznikov. *J. Mater. Chem.*, 2012, **22**, 286; d) T. Seki, S. Nagano and M. Hara, *Polymer*, 2013, **54**, 6053.
4. a) A. Natansohn and P. Rochon, *Chem. Rev.*, 2002, **102**, 4139; b) Y. Zhao and T. Ikeda eds., *Smart Light-Responsive Materials: Azobenzene-containing Polymer and Liquid Crystals*, A John Wiley & Sons Ltd, New Jersey, 2009. c) Q. Li ed., *Liquid Crystals Beyond Displays: Chemistry, Physics, and Applications*, John Wiley & Sons Ltd, New Jersey, 2012.
5. K. Ichimura, S. Morino and H. Akiyama, *Appl. Phys. Lett.*, 1998, **73**, 921.
6. M. Han, S. Morino and K. Ichimura, *Macromolecules,* 2000, **33**, 6360
7. M. Han and K. Ichimura, *Macromolecules,* 2001, **34**, 90.
8. M. Han and K. Ichimura, *Macromolecules,* 2001**, 34**, 82.
9. K. Ichimura, S. Iwata, S. Mochizuki, M. Ohmi and D. Adachi, *J. Polym. Sci. Part A: Polym. Chem.*, 2012, **50**, 4094.
10. K. Ichimura, *J. Mater. Chem. C*, 2014, **2**, 641.
11. (a) G. Talsky, L. Mayring and H. Kreuzer, *Angew. Chem., Int. Ed.*, 1978, **17**, 785; (b) J. Karpinska, *Talanta*, 2004, **64**, 801; (c) F. S. Rojas and C. B. Ojeda, *Anal. Chim. Acta*, 2009, **635**, 22.
12. A. Mishra, R. K. Behera, P. K. Behera, B. K. Mishra and G. B. Behera, *Chem. Rev.*, 2000, **100**, 1973.
13. H. Menzel, B. Weichart, A. Schmidt, S. Paul, W. Knolls, J. Stumpe and T. Fischer, *Langmuir,* 1994, **10**, 1926.
14. X. Tong, L. Cui and Y. Zhao, *Macromolecules,* 2004, **37**, 3101.

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