

Temperature Sensitive Swelling of Poly(N-isopropylacrylamide) Brushes with Low Molecular Weight and Grafting Density

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Supporting Informations

In a recent paper of Maeda FTIR spectra on highly concentrated PNIPAAm D₂O solutions [34] were analyzed applying curve fitting analysis of the Amide I and Amide II band lineshape by band components (presumably Gaussian/Lorentzian ones, respectively). The spectrum of PNIPAAm recorded at $T = 25^{\circ}\text{C} < T_p$ (referred as “phase transition temperature”) could be fitted by a single component at 1625 cm^{-1} , while the spectrum at $T = 40^{\circ}\text{C}$ ($T > T_p$) could be fitted by two components at 1650 and 1625 cm^{-1} . According to [32] based on density functional theory (DFT) the 1625-cm^{-1} component was assigned to H-bonding carbonyl groups to two water molecules and the 1650-cm^{-1} component to singly H-bonding carbonyl groups to another amide group or one water molecule.”

We like to share this concept for the application on PNIPAAm brush films and fitted our spectra including also the $\nu_a(\text{CH}_3)$ and the Amide II band using a protocol described earlier therein [1]. In the Fig. 11a results on curve fitting of the ATR-FTIR spectra recorded at $T=22^{\circ}\text{C}$ and $T=44^{\circ}\text{C}$ for the fitted range between 1700 and 1500 cm^{-1} are given. For both temperatures two Amide I (1654 and 1628 cm^{-1}) and two Amide II (1558 and 1537 cm^{-1}) components were needed to obtain appropriate fits. Note that applying H₂O instead of D₂O Amide I band (components) have blue shifts to slightly higher wavenumbers and Amide II band is *not* red shifted by around 100 cm^{-1} . Hence we assign the 1654- and 1537-cm^{-1} components to amide groups of high internal and low external hydrogen bonding degree to water and the 1628- and 1558-cm^{-1} components to those with low internal and high external hydrogen bonding degree to water. Since two Amide I or Amide II components, respectively, were needed to fit the low and high T-spectrum, qualitatively it can be concluded, that PNIPAAm brush films at high T ($T > T_p$) still contain a considerable amount of

external hydrogen bonding to water. Also from this it can be concluded, that at low T ($T < T_P$) PNIPAAm brushes still contain a considerable amount of internal hydrogen bonding. In contrast Maeda [32] needed only one component to fit the low temperature spectrum of PNIPAAm in solution, from which unlike the brush state a complete hydration of PNIPAAm in the solution state can be derived.

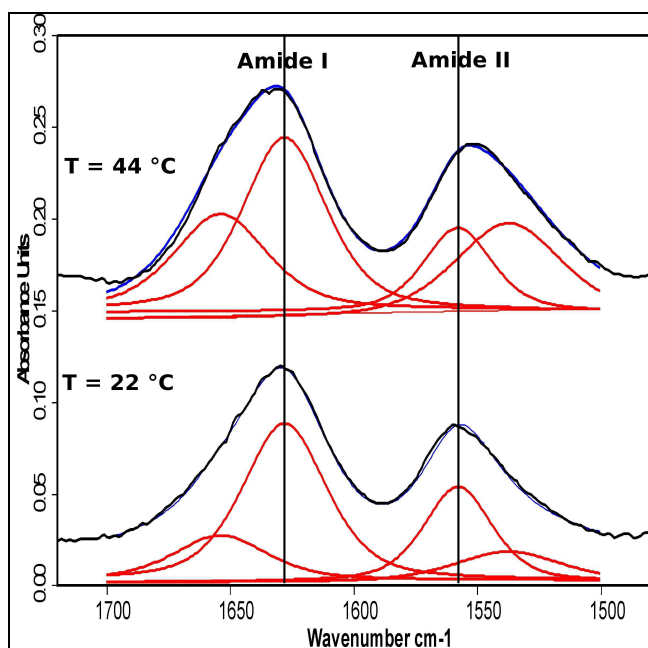


Fig. 11a. Results on curve fitting the Amide I ($1654, 1628 \text{ cm}^{-1}$) and Amide II ($1558, 1537 \text{ cm}^{-1}$) band lineshape in ATR-FTIR spectra of the PNIPAAm (132 kg/mol) brush in contact to PBS buffer at $T=22^\circ\text{C}$ (bottom) and $T=44^\circ\text{C}$ (top) with two components. Original (black), fitted (blue) spectra and components (red) are shown.

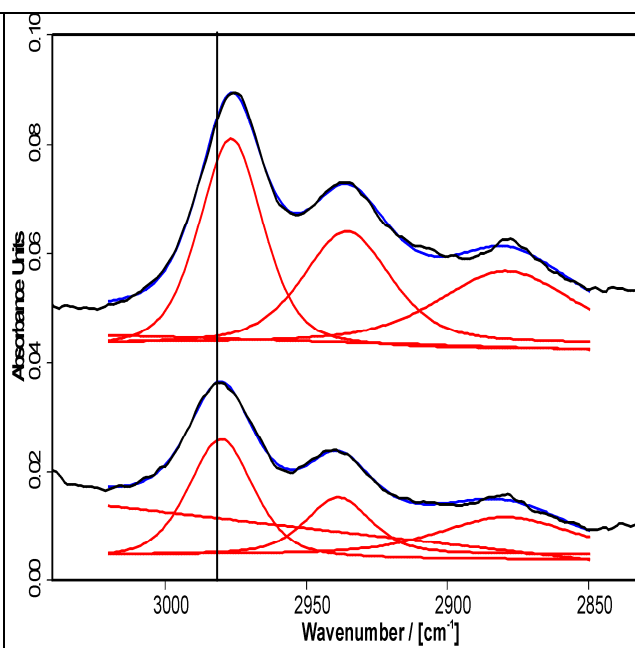


Fig. 11a. Results on curve fitting the $v(\text{CH})$ band lineshape in ATR-FTIR spectra of the PNIPAAm (132 kg/mol) brush in contact to PBS buffer at $T=22^\circ\text{C}$ (bottom) and $T=44^\circ\text{C}$ (top). Original (black), fitted (blue) spectra and components (red) are shown.

Analogously to the Amide I band region lineshape analysis was applied on the $v(\text{CH})$ region of the ATR-FTIR spectra, which is shown in the Fig. 11b. Unlike the Amide I and Amide II bands, only one component at 2980 cm^{-1} was found for the $v(\text{CH}_3)$ band of the low T ATR-FTIR spectrum and one at 2976 cm^{-1} for the high T spectrum. For the spectra in between both components at 2980 and 2976 cm^{-1} were found. From this finding we conclude that the methyl groups of PNIPAAm are

influenced by the type of hydrogen bonding (external/internal) but unlike the amide groups a mixture prevails neither at low nor at high temperatures.

In the Fig 12a the integrals of the normalized $\nu_a(\text{CH}_3)$, Amide I and Amide components which increase by temperature (“hot components”) and in Fig. 12b those which decrease by temperature (“cold components”) are plotted versus T. For all components rather continuous courses, like that shown in the Fig. 10b for the wavenumber positions, were found, which is supported by theoretical predictions, that the collapse of the surface-grafted polymer brushes proceeds continuously with increasing temperature [37, 38].

