Fluorescence Resulting from π -stacking in Polystyrene Solutions

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doi:10.5618/chem.2011.v1.n1.9 || Received: 20-10-2011, Accepted: 5-11-2011, Available online: 13-11-2011

Abstract

The fluorescence of polystyrenes solutions are reported in three different concentrations with one in semi-diluted regime and two in diluted regime. With the excitation energy of 260 nm, only the widely studied monomer fluorescence emission near 285 nm and excimer fluorescence emission near 330 nm are observed. With the excitation energies at 277nm and longer wavelengths, the unexpected emissions in the longer wavelength range 350-480 nm that was recently discovered in polystyrene fine particles are also found to appear in polystyrene solutions, but with fewer structures and major peaks in different wavelengths. The major emissions shift from the region of 320-390 nm in polystyrene fine particles to the region of 380-450 nm in solutions. The excitation spectrum of the emissions at longer wavelength reveals much broader absorption bands with fewer resolved structures in polystyrene solutions than the absorption bands recorded in fine particles. Considering the simplicity of polystyrene molecules and previous studies, aromatic-aromatic (or π -stacking) interactions are believed to be the major driving forces for the formation of phenyl dimers and multimers from which the new emissions in longer wavelengths originate. The mechanism of the formation of these phenyl multimers in polystyrene solutions remains unsolved in this study, however the new fluorescence emissions discovered will contribute to the study of π -stacking interactions, and can also be a powerful probe for monitoring molecular motions and ordered structures of polystyrene molecules or other aromatic macromolecules in solutions.

Keywords: polystyrene solutions; aromatic-aromatic (or π -stacking) interactions; fluorescence; phenyl multimers.

1. Introduction

As one of the most general macromolecules, polystyrene's photophysical properties have been investigated extensively using fluorescence spectroscopy. Two types of fluorescence emission are reported in

polystyrene systems: monomer fluorescence emission near 285 nm due to fluorescence from a single phenyl group in polystyrene, and excimer fluorescence emission near 330 nm from an excited state complex of two phenyl groups[1]. Of special interest is excimer emission, especially the ratio of the excimer to monomer fluorescence intensities, I_E/I_M , has been used to characterize the fluorescence properties, intramolecular and intermolecular interactions as well as conformational properties of polystyrene [2-8].

Recently I reported new structured fluorescence emissions in longer wavelengths (360-460 nm) than polystyrene excimer emission in polystyrene fine particles and cast film [9]. The detailed information about the growth of these new emissions in polystyrene fine particles under ambient conditions and vacuum have also been discussed and documented [10], as well as the energy transfer between different phenyl chromophores: monomers, dimers and multimers. This work reports that similar fluorescent phenomena occurred in long wavelengths as discovered in polystyrene fine particles and cast film can be also observed in polystyrene solutions.

2. Materials and methods

Spectroscopic-grade methanol and tetrahydrofuran (THF) were used without further purification. Polystyrene samples purchased from Polymer Source were of narrow molecular weight distribution standards. The molecular weights and polydispersities were $M_w=130,000$ and $M_w/M_n=1.04$, respectively. The following concentrations of polystyrene solutions in THF were prepared: 1) 0.28 g/ml (S1), 2) 1.0×10^{-2} g/ml (S2) and 3) 1.2×10^{-3} g/ml (S3), respectively. Quartz 1-cm path length cells with stoppers to prevent evaporation were used for all measurements. With solution S1 of high concentration, gentle heating (55° for a week) was employed to facilitate dissolution and equilibrated. The low concentration solutions S2 and S3 were kept at room temperature for a week to equilibrate.

Fluorescence spectra of the polystyrene solutions were obtained with a Jobin-Yvon SPEX F212 using the

front-face mode at room temperature ($\sim 25^\circ$). The slit widths were set to 1.0 nm for all measurements. Some reported spectrum were an average of a few separate scans to reduce noise.

3. Results and discussion

3.1 Fluorescence emission spectra As previously reported by many researchers, **Fig.1** demonstrates the fluorescence emissions at $\lambda_{\text{ex}} = 260$ nm of the studied polystyrene solutions S1, S2, and S3 are centered at the two peaks near 285 and 330 nm which have been assigned to a phenyl monomer singlet and excimer emission, respectively. In the studied polystyrene solutions, the excitation of single phenyl group at 260 nm does not result in the fluorescence emissions in longer wavelengths as observed for the polystyrene fine particles [9] as shown in grey curve. The emission profile of the concentrated solution S1 does show some tiny shoulders in the wavelength range of 350-450 nm but they are hard to be discerned from noise.

Fig.1 The fluorescence emission spectra at $\lambda_{\text{ex}} = 260$ nm of the studied polystyrene solutions in THF (S1: 0.28 g/ml, S2: 1.0×10^{-2} g/ml, and S3: 1.2×10^{-3} g/ml), compared with the rescaled emission spectrum of the polystyrene fine particles (P1) after vacuum drying [9]. The spectrum of the polystyrene fine particle is rescaled for comparison.

However, when excited with 277 nm wavelength light (**Fig.2**), the polystyrene solutions exhibit fluorescence emissions in longer wavelength region as the polystyrene fine particles [9], but with different emission maxima and fewer structures. The fluorescence emissions of the low concentration polystyrene solutions S2 and S3 are two structureless broad peaks, while the emissions of the high concentration solution S1 show

some structured peaks at the same wavelengths observed for the polystyrene fine particles, especially at 347 nm, 355 nm, 365 nm, and 404 nm.

It has been discussed the fluorescence emissions in longer wavelengths in polystyrene fine particles are emit from the phenyl multimers formed under the driving forces of chain relaxation during solvent evaporation, hydrophobic interactions during reprecipitation and powerful aromatic-aromatic interactions [9] between phenyl groups. Among the three driving forces, only aromatic-aromatic interactions can be applied to the polystyrene solutions. S1 solution's concentration belongs to the semi-dilute regime but is only slightly lower than the limit of the concentrated regime C^* [11]. The semi-dilute regime is characterized by entanglement interactions, and the rotational motion is restricted by interactions with surrounding filaments. Since the S1 concentration is close to the concentrated regime, the polystyrene must interact with one another strongly and the entangled networks are large. In these entangled networks, surrounding polystyrene chains impose topological constraints on one another, inhibiting their Brownian motion. The aromatic-aromatic interactions then can overcome the molecular motion and orient the phenyl groups to form phenyl dimers and multimers. Some of these dimers and multimers must be in similar geometries as those formed in polystyrene fine particles, and so that the emission fine structures at longer wavelength side of excimer emission peak at 347 nm, 355 nm, 365 nm, and 404 nm that are observed in polystyrene fine particles [9] are also observed in the S1 solution.

Fig.2 The fluorescence emission spectra at $\lambda_{\text{ex}} = 277$ nm of the studied polystyrene solutions in THF (S1: 0.28 g/ml, S2: 1.0×10^{-2} g/ml, and S3: 1.2×10^{-3} g/ml), compared with the rescaled emission spectrum of the polystyrene fine particles (P1) after vacuum drying [9].

Both the **S2** and **S3** solutions are in the dilute regime, with the concentration of **S2** solution only slightly lower than the lower limit of semi-dilute range C^* , but the concentration of **S3** solution ~ 10 times lower than C^* [11]. In the dilute solution such as **S3**, the polystyrene coils are statistically isolated and their encounters are infrequent. The chances for phenyl groups of different chains to come into a close proximity of forming multimers are small. Consequently the emissions of the **S3** diluted solution in longer wavelength range 370-400nm are weak compared with the emissions from the other two solutions. As the **S2** solution belongs to the dilute regime but in a much higher concentration that is close to the C^* , the emission profile of **S2** solutions resembles that of **S1** solution but lacks the fine structures in the region of 340-380 nm. As the concentrations increase, the relative intensities of the broad emission peak centered at ~ 400 nm become stronger. It is interesting that the most intense fluorescence emissions in polystyrene fine particles occur in the wavelengths between the two major broad peaks centered at 330 nm and 400nm in polystyrene solutions.

As shown in **Fig. 3**, with excitation light at a longer wavelength of 290 nm, the fluorescence emissions in the polystyrene solutions all show obvious fine structures in the region of 320-379nm to different extents. The intensity ratio of the emission band centered near 400nm to other emissions in the range of 320-370 nm becomes much stronger in all the three solutions, with largest ratio from the diluted **S2** solution but not the most concentrated **S1** solution. Although the fluorescence intensities decrease dramatically as the concentration decrease from **S1** to **S2** and then **S3** as shown in the inserted figure in **Fig.3**. The major emissions shift from the region of 320-390 nm in polystyrene fine particles to the region of 380-450 nm in solutions. This is an interesting observation since the emissions in longer wavelengths are from larger multimers with more interacting phenyl groups. This indicates that the population ratio of excited larger multimers to excimers is larger in polystyrene solutions than in fine particles, or the energy transfer from excimers to larger multimers is more efficient in polystyrene solutions than in fine particles.

When excited with 340 nm light, as shown in **Fig. 4**, the concentrated solution **S1** shows a broad emission without structured emissions observed in the polystyrene fine particles, neither the **S2**

solution. However the emission profile of the most diluted **S3** solution seems to show some structures.

Fig.3 The normalized fluorescence emission spectra at $\lambda_{\text{ex}} = 290$ nm of the studied polystyrene solutions in THF (**S1**: 0.28 g/ml, **S2**: 1.0×10^{-2} g/ml, and **S3**: 1.2×10^{-3} g/ml), compared with the rescaled emission spectrum of the polystyrene fine particles (**P1**) after vacuum drying [9]. The inserted figure is the non-scaled spectra of the three solutions.

Fig.4 The normalized fluorescence emission spectra at $\lambda_{\text{ex}} = 340$ nm of the studied polystyrene solutions in THF (**S1**: 0.28 g/ml, **S2**: 1.0×10^{-2} g/ml, and **S3**: 1.2×10^{-3} g/ml), compared with the rescaled emission spectrum of the polystyrene fine particles (**P1**) after vacuum drying [9]. The inserted figure is the non-scaled spectra of the three solutions.

The fluorescence emission spectrum should be independent of the excitation wavelength, due to the partial dissipation of excitation energy during the excited-state lifetime. However the emission profiles with different excitation energies shown in **Figures 1-4** are all different, especially for the excitation energies of 260, 277 (or 290) and 340 nm. This indicates that the different excitation energies can either excite directly the phenyl multimers in different geometries resulting in different emissions, or lead to the energy transfer to different multimers with different emissions (indirect excitation). **Fig. 5** shows the comparisons of fluorescence emission profiles at different excitation energies for each polystyrene system: S1 solution, S2 solution, S3 solution, and fine particles after vacuum drying. The relative intensities of the emissions at different excitation energies in each system are different from each other. In the concentrated S1 solution, the excitation energy of 290 nm leads to the most intense emissions, and then the fluorescence decreases in the order of 340 nm, 277 nm and 260 nm excitation energies. It can be concluded that the sum of fluorescence emit from direct excitation of multimers with 290 nm and indirect excitation of multimers through the energy transfer is strongest in the S1 solution. However, in the S2 solution, the most intense fluorescence is excited with 277 nm light. Furthermore, in the S2 solution, the two excitation energies of 277 nm and 340 nm can lead to the same fluorescence intensity for the emission centered at 400 nm. This implies that the two excitation energies can excite the same total number of phenyl multimers leading to the emission centered at 400 nm through direct excitation and indirect excitation via energy transfer. In the diluted S3 solution, the major emissions are the excimer emission at 330 nm. As discussed above, the concentration of the S3 solution is diluted enough so that the polystyrene coils are statistically isolated and their encounters are infrequent. The chances for phenyl groups of different chains to come into a close proximity of forming multimers are small. The much weaker emissions in longer wavelength with the excitation energies at 290 nm and 340 nm compared with other solutions are supposedly to emit from phenyl multimers from the same polystyrene chains only. The Brownian motion of polystyrene chains are much faster in dilute solution which is hard to be overcome by aromatic-aromatic interactions between different phenyl rings from the same polystyrene chain. In the polystyrene fine particles after extensive vacuum drying, the emission profiles at different excitation energies are in similar intensity scale. The emission centered around 325 nm are much stronger with the excitation energy of 260 nm than that with the excitation

energies of 277 nm or 290 nm. This implies that the emission at 325 nm in fine particles is possibly from the excimers formed between one excited singlet phenyl ring and the other phenyl ring in ground state.

Fig.5 The comparison of fluorescence emission spectra at $\lambda_{\text{ex}} = 260$ nm (curves 1, thin dark), $\lambda_{\text{ex}} = 277$ nm (curves 2, thick dark), $\lambda_{\text{ex}} = 290$ nm (curves 3, thin grey) and $\lambda_{\text{ex}} = 340$ nm (curves 4, thick grey) for the studied polystyrene solutions in THF (S1: 0.28 g/ml, S2: 1.0×10^{-2} g/ml, and S3: 1.2×10^{-3} g/ml), as well as the polystyrene fine particles (P1) after vacuum drying [9]. The emission spectral intensities of the diluted solution S3 at $\lambda_{\text{ex}} = 290$ and 340 nm are both multiplied by 6.

Excimers can be formed through a number of pathways: 1) excitation of ground state dimers to form excimers directly; 2) excitation of an isolated phenyl group

followed by intramolecular motion such as chain recoiling or bond rotation to form an intramolecular excimer with another ground-state phenyl group in a suitable position, 3) or by chain diffusion to form an intermolecular excimer, 4) or by energy migration to an excimer-forming site [12] [13]. The quenching study showed that energy migration does not occur in dilute solution of polystyrene [14]. Masegosa *et al* concluded that recoiling of long polystyrene chains does not bring pairs of aromatic rings from non-neighbouring monomer units together to form excimers [15]. In general, the excited multi-mers leading to the fluorescence emissions at longer wavelengths could be formed in similar pathways as excimers described above but no studies were reported to my knowledge. It was proposed that in polystyrene fine particles, the fluorescence emissions at 347 and 365 nm are from the excited phenyl trimers, while the emissions at 383, 404, and 426 nm are emit by the excited phenyl tetramers [10]. In the studied polystyrene solutions in this work, the fluorescence emissions covered the 347 and 365 nm region (trimers) are the region exhibited fine structures at the excitation energies of 277 nm (**Fig. 2**) and 290 nm (**Fig. 3**). The emissions spanned 383-426 nm (tetramers) are the structureless broad peaks in the polystyrene solutions. If these emissions are from the corresponding the same excited phenyl multimers in the polystyrene solutions as proposed for polystyrene fine particles, these excited multimers must have more freedom in rotation and other motions resulting in less distinct stable geometries. Consequently, the emission fine structures are absent in solutions.

3.2 Fluorescence excitation spectra The fluorescence excitation spectra of the excimer emission at 330 nm in the polystyrene solutions S1, S2, and S3 shown in **Fig. 6** reveals that the excitation energies leading to excimer fluorescence are centered at 286 nm, 276 nm and 266 nm, respectively. There are red-shifts with increasing solution concentrations. The red-shift results in unexpected fluorescence intensity order at $\lambda_{\text{ex}} = 260$ nm in the three solutions. It explains why the intensities of fluorescence emissions at the excitation energy of 260 nm decrease in the order of S3, S1 and S2 (**Fig. 1**). It is interesting that the absorption peaks shown in the excitation spectra of the three solutions all have corresponding absorption peaks in the same wavelengths in the polystyrene fine particles (grey curve). This indicates the excimers with different geometries formed in the three different solutions can also be formed in the polystyrene fine particles.

Fig. 6 The fluorescence excitation spectra at $\lambda_{\text{em}} = 330$ nm of the studied polystyrene solutions in THF (S1: 0.28 g/ml, S2: 1.0×10^{-2} g/ml, and S3: 1.2×10^{-3} g/ml), compared with the rescaled excitation spectrum of the polystyrene fine particles (P1) after vacuum drying [9].

The fluorescence excitation spectra at $\lambda_{\text{em}} = 419$ for emissions at longer wavelengths in the polystyrene solutions S1, S2, and S3 are presented together in **Fig. 7**. The excitation spectral intensity of the diluted solution S3 is multiplied by a factor of 10 for a clearer view. Compared with the corresponding excitation spectrum of polystyrene fine particles [9], the excitation spectra of the three polystyrene solutions appear as broad peaks without resolvable fine structures. However the absorption peaks in polystyrene solutions and fine particles are spanned by a similar energy region of 270-400 nm. In solutions, the absorption bands at 270-330 nm have much stronger contribution than the absorption band at 330-400 nm to the emissions in longer wavelengths (the broad peak at 360-450 nm). However in the polystyrene fine particle, the contribution from the absorption band centered at 340 nm is the greatest while the contributions from other absorption bands ranging from 270 nm to 380 nm are similar. It was proposed that in polystyrene fine particles, the absorption bands centered at 278, 282, 285, 292, 296 and 302 nm are caused by the phenyl dimers, the absorption peaks centered at 325, 332, 340, and 347 nm are from the phenyl trimers, while the absorption peaks at 360 and 380 nm are belong to the phenyl tetramers [10]. In the studied polystyrene solutions, however, the maximum absorption band is around 309 nm, a wavelength that is between the absorption centers of the least stable proposed dimer (302 nm) and the most stable proposed trimer (325 nm) in polystyrene fine

particles[10]. No structures are proposed for the absorption band centered around 309 nm in polystyrene fine particles [10], however, as shown in **Fig.16** of energy transfer diagram [10], this absorption band have relative weak contribution to the emissions centered around 347, 365, 383, and 404 nm in polystyrene fine particles that are proposed to be emit from the excited phenyl trimers (347 and 365) and phenyl tetramers (383 and 404), respectively. Therefore the absorption band centered at 309 nm in solution possibly belongs to phenyl trimer(s). The emission profiles at $\lambda_{ex} = 309$ nm of the polystyrene solutions are not shown here but they resembles the profiles at $\lambda_{ex} = 340$ nm shown in **Fig. 4**.

Fig. 7 The fluorescence excitation spectra at $\lambda_{em} = 419$ nm of the studied polystyrene solutions in THF (S1: 0.28 g/ml, S2: 1.0×10^{-2} g/ml, and S3: 1.2×10^{-3} g/ml), compared with the rescaled excitation spectrum of the polystyrene fine particles (P1) after vacuum drying [9]. The excitation spectral intensity of the diluted solution S3 is multiplied by 10.

Fig. 8 shows the comparisons of excitation spectra at $\lambda_{em} = 330$ nm and $\lambda_{em} = 419$ nm for all the studied polystyrene solutions S1, S2, and S3, as well as the polystyrene fine particles. The comparisons present a direct visualization of how much the excimer emission contributes to the emission in longer wavelength near 419 nm through energy transfer. The larger overlap between the excitation spectra at $\lambda_{em} = 330$ nm and $\lambda_{em} = 419$ nm, the more efficient energy transfer from the excimer emission to the emission at longer wavelengths. In the studied polystyrene solutions, the order is shown in an expected order: $S1 > S2 > S3$. As concentration increases, the polystyrene chains have more chance to entangle, and thus phenyl groups have higher proba-

bility to come into close proximity to interact through aromatic-aromatic interactions to form more fluorophores that can re-absorb of the emitted light by the excimers.

Fig. 8 The comparison of fluorescence excitation spectra at $\lambda_{em} = 330$ nm (light curves) and $\lambda_{em} = 419$ nm (thick curves) for the studied polystyrene solutions in THF (S1: 0.28 g/ml, S2: 1.0×10^{-2} g/ml, and S3: 1.2×10^{-3} g/ml), as well as the polystyrene fine particles (P1) after vacuum drying [9]. The excitation spectral intensity of the diluted solution S3 at $\lambda_{em} = 419$ nm is multiplied by 10.

4. Summary

The unexpected fluorescence emissions at longer wavelengths (350-480 nm) than excimer emission in polystyrene solutions are reported the first time. Compared with the similar fluorescence phenomena observed in polystyrene fine particles [9-10], these emissions are believed to emit from the excited phenyl multimers mostly driven by aromatic-aromatic (or π -stacking) interactions between the phenyl grounds. Different from the polystyrene fine particles after vacuum drying, the excitation at 260 nm does not lead to the fluorescence emissions in longer wavelengths in the

studied polystyrene solutions. Only the excitations with 277 nm light or light in longer wavelengths can result in the unexpected emissions in longer wavelengths. Although the fluorescence emissions and their corresponding excitation spectra span the same energy ranges in polystyrene solutions and fine particles, both the fluorescence profiles and excitation profiles of the studied polystyrene show much fewer resolved fine structures than the corresponding profiles of dried polystyrene fine particles. Furthermore the major emissions shift from the region of 320-390 nm in polystyrene fine particles to the region of 380-450 nm in solutions. This implies larger population ratio of excited larger multimers to excimers in polystyrene solutions than in fine particles, or more efficient energy transfer from excimers to larger multimers in polystyrene solutions than in fine particles. The major absorption bands contributed to the unexpected emissions in longer wavelengths are located at 309 nm in solutions, and at 340 nm in fine particles, respectively. Both absorption bands are likely due to the excitation of phenyl trimers.

The polystyrenes solutions reported in this work are in two different concentration regimes: S1 in semi-diluted regime with concentration close to the concentrated regime, S2 and S3 in diluted regime with S2 concentration close to the lower limit of semi-dilute regime and S3 is ~10 times lower. They exhibit different emission and excitation profiles. With topological constraints imposed by the surrounding polystyrene chains on one another in the entangled networks of the concentrated S1 solution to inhibit the Brownian motion, the aromatic-aromatic interactions can lead to formation of phenyl multimers in more distinct structures. Consequently the emissions of the S1 solutions show most resolved fine structures that are observed in polystyrene fine particles. In the diluted S3 solution, the unexpected emissions in longer wavelength are much weaker since polystyrene coils are statistically isolated and the aromatic-aromatic interactions between different phenyl rings from the same polystyrene chain need to compete with fast Brownian motion of polystyrene chains. Furthermore the excitation spectra reveal that energy transfer between the excimer emissions and phenyl multimers is more efficient in concentrated solutions. The mechanism of the formations of these excited phenyl multimers is not clear. Further investigations in polystyrene solutions in a wider range of concentrations and different solvents or with polystyrene in different molecular weights and configurations (such as isotactic or syndiotactic) might contribute to the unveiling of the mechanism.

The new fluorescence emissions discovered in this work will contribute to deeper investigation of π -stacking interactions, and can also be a powerful probe for monitoring molecular motions and ordered structures of polystyrene molecules or other aromatic macromolecules in solutions.

References

- [1] Toyochi Tanaka, Experimental methods in polymer science: modern methods in polymer research and technology, *Academic Press*, **2000**.
- [2] Vala, M. T.; Haebig, J.; Rice, S. A. *J. Chem. Phys.* **1965**, 43886.
- [3] Nishihara, T. and Kaneko, M. *Makromol. Chem.* **1969**, 124, 84.
<http://dx.doi.org/10.1002/macp.1969.021240109>
- [4] Frank, C. W.; Gashgari, M. *Macromolecules* **1979**, 12, 163. <http://dx.doi.org/10.1021/ma60067a038>
- [5] Roots, J.; Nyström, B. *Eur. Polym. J.* 1979, 15, 1127.
[http://dx.doi.org/10.1016/0014-3057\(79\)90047-8](http://dx.doi.org/10.1016/0014-3057(79)90047-8)
- [6] Torkelson, J. M., Lipsky, S., Tirrell, M. and Tirrell, D. A. *Macromolecules* **1983**, 16, 326.
<http://dx.doi.org/10.1021/ma00236a031>
- [7] Renyuan, Q.; Ti Cao, *Polym. Commun.* **1986**, 27, 169.
- [8] Tsai, F.-J.; Torkelson, J.M., *Polymer*, **1988**, 29, 1004-1009.
[http://dx.doi.org/10.1016/0032-3861\(88\)90007-9](http://dx.doi.org/10.1016/0032-3861(88)90007-9)
- [9] Kuo, A. *CheM*, **2011**, 1, 1-8.
<http://dx.doi.org/10.5618/chem.2011.v1.n1.1>
- [10] Kuo, A. *CheM*, **2011**, 1, 40-51.
<http://dx.doi.org/10.5618/chem.2011.v1.n1.6>
- [11] Iwao Teraoka, Polymer solutions: an introduction to physical properties, *John Wiley and Sons*, **2002**.
- [12] Birks, J. B., Ed. Organic Molecular Photophysics, Vol. 1 and 2, *Wiley: New York*, **1975**.
- [13] Cowan, D. O.; Drisko, R. L. Elements of Organic Photochemistry; Plenum: NewYork, **1976**.
- [14] Maccallum, J. R.; Rudkin, A. L.; *European Polymer Journal* **1981**, 17, 953-956.
[http://dx.doi.org/10.1016/0014-3057\(81\)90221-4](http://dx.doi.org/10.1016/0014-3057(81)90221-4)
- [15] Masegosa, R. M.; Hernández-Fuentes, I.; Fernández de Piérola, I.; Horta, A., *Polymer*, **1987**, 28, 231-235.
[http://dx.doi.org/10.1016/0032-3861\(87\)90409-5](http://dx.doi.org/10.1016/0032-3861(87)90409-5)