

Supramolecular polymer interactions based on the alternating copolymer of styrene and maleimide

Citation for published version (APA):

Lange, R. F. M., & Meijer, E. W. (1995). Supramolecular polymer interactions based on the alternating copolymer of styrene and maleimide. *Macromolecules*, 28(3), 782-783. <https://doi.org/10.1021/ma00107a016>

DOI:

[10.1021/ma00107a016](https://doi.org/10.1021/ma00107a016)

Document status and date:

Published: 01/01/1995

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Supramolecular Polymer Interactions Based on the Alternating Copolymer of Styrene and Maleimide

Ronald F. M. Lange and E. W. Meijer*[†]

DSM Research, P.O. Box 18,
6160 MD Geleen, The Netherlands

Received August 17, 1994

Revised Manuscript Received November 22, 1994

Biomacromolecules represent one of the most fascinating areas of supramolecular architecture and self-assembly based on multiple-hydrogen bonding, with the DNA double helix as the most prominent example. Despite the importance of macromolecules in natural systems, research in the field of supramolecular chemistry is mainly focused on low molecular weight molecules,¹ while self-assembly of macromolecules is investigated in detail for liquid crystallinity, hydrophobic interactions, amphiphilic structures and rotaxanes.² Recently, Lehn et al. introduced the concept of using well-defined secondary interactions based on hydrogen bonding in the synthesis of liquid crystalline polymers, in which the repeating units are linked by triple-hydrogen bonding instead of by covalent bonding.³ Furthermore, Fréchet et al. studied the liquid-crystalline state obtained by the supramolecular side-chain interactions of polyacrylates with stilbazoles or polysiloxanes,⁴ while Stadler reported on supramolecular polymer networks consisting of cooperative hydrogen bonding between (4-carboxyphenyl)urazole units grafted on polybutadiene.⁵

The use of secondary interactions in the formation of polymer blends is a well-accepted strategy; donor-acceptor complexes,⁶ ion pairs,⁷ and hydrogen bonding⁸ represent some successful examples. In this communication, we report on our results of the supramolecular interactions between the alternating copolymer of styrene and maleimide, **1**, with melamine, **2**, and of **1** with the copolymer of styrene and 2,4-diamino-6-vinyl-1,3,5-triazine, **3**. The interactions between **1** and either **2** or **3** are based on the concept of triple-hydrogen bonding as shown in Figure 1.

Results and Discussion. In order to study multiple-hydrogen bonding in polymer blends, we have synthesized the complementary copolymers **1** and **3** and used commercially available **2**. The alternating, atactic copolymer of styrene and maleimide, **1**, is obtained by the radical polymerization of styrene and maleimide in butanone at 60 °C with AIBN as initiator.⁹ DEPT-¹³C-NMR spectroscopy reveals that alternation over 95% is obtained. The atactic, amorphous **1** ($M_n = 77 \times 10^3$, $D = 2.1$, as determined by GPC, Ultrastyrigel, THF + 10% CH₃COOH and polystyrene as standards) possesses a glass transition temperature (T_g) of 250 °C and starts to decompose at temperatures above 350 °C. Polymer **3** is obtained as a random, atactic copolymer by the radical polymerization of styrene and 2,4-diamino-6-vinyl-1,3,5-triazine in DMSO at 60 °C with AIBN as initiator.¹⁰ The resulting polymer **3** ($M_n = 14 \times 10^3$, $D = 2.8$, as determined with GPC, nucleosil-7-OH, hexafluoro-2-isopropanol + 0.2% CF₃COOK and polystyrene as standards) is amorphous and exhibits a T_g of 220 °C, whereas the decomposition temperature is above 360 °C.

[†] Present address: Laboratory of Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

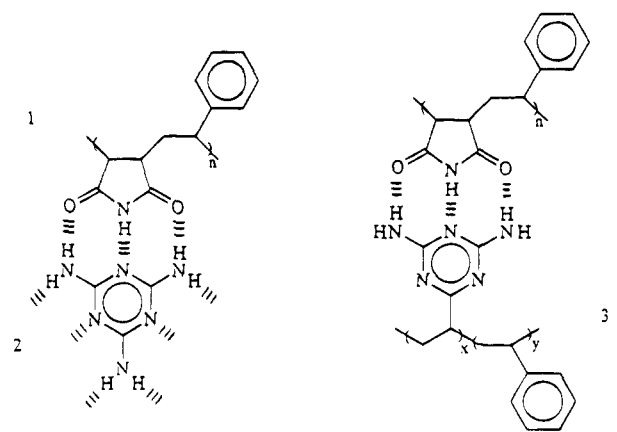


Figure 1.

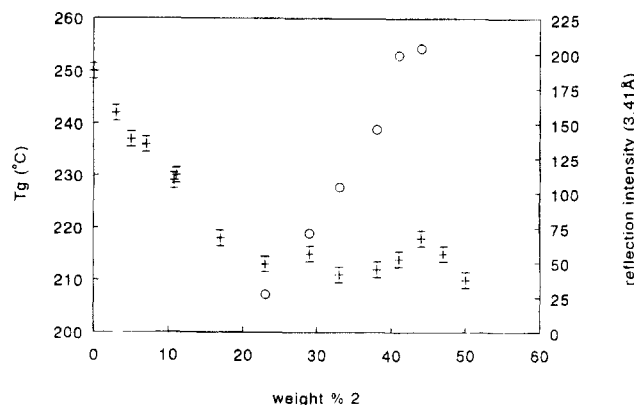


Figure 2. Dependence of T_g (+) and melamine reflection intensity (O) on the concentration of melamine in the alternating copolymer of styrene and maleimide.

Blending of **1** with various amounts of melamine, **2**, is carried out in the melt, using an extruder, at 320 °C for 2 min. The dependence of T_g on the concentration of melamine is given in Figure 2. Addition of melamine results in a dramatic decrease of the T_g , up to melamine concentrations of 20% (w/w), at which it levels off at around 215 °C. In order to get more insight into the state of mixing of **1** with **2**, powder diffraction X-ray analysis of the prepared samples has been performed. Reflections at 3.41 Å (Cu K α radiation) for crystalline, undissolved, melamine are detected only at melamine concentrations of 23% (w/w) and higher.¹¹ Extrapolation of the intensity of reflection to zero shows that no melamine crystals are present at concentrations lower than 19.7% (w/w) of **2**, as is shown in Figure 2. The figure shows, as well, that this point coincides with the onset of T_g stabilization. Therefore, it is concluded that melamine, known as a compound barely soluble in any organic solvent, is molecularly dissolved in **1** up to an imide:melamine ratio of 2.6 :1.¹² Hence, it is proposed that one melamine molecule interacts with three imide units of the polymer, leading to a three-dimensional hydrogen-bonded polymer network, hereby disrupting the imide-imide interaction. Investigations to explain the decrease in T_g and the exact nature of the complex are in progress.

Preliminary model studies of the complexation of **2** with low molecular weight imides have been performed to study these supramolecular polymer structures. X-ray crystal structures of **2** with succinimide and of **2** with glutarimide reveal that a 1:1 sheetlike and a 2:1 herringbone structure are formed, respectively. The

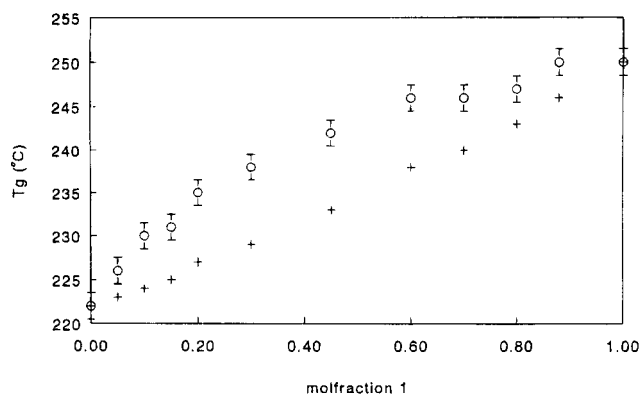


Figure 3. T_g (O experimental, + calculated Flory-Fox) as a function of the composition of the blend of **1** and **3**.

availability of the acceptors and donors for hydrogen bonding is strongly influenced by subtle differences in the molecular structure of the imide. Similar subtle effects are reported for model studies of supramolecular sheets of melamine and cyanuric acid.¹³

In order to extend our approach of multiple-hydrogen bonding to polymer-polymer interactions, we have blended **1** with **3**. The latter polymer with a diamino-triazine unit is complementary to the imide functionalized **1**, as is shown in Figure 1. In this case, the blends are obtained by dissolving **1** and **3** in DMSO, followed by coprecipitation in water. DSC and DMA analyses of the resulting blends show a single T_g for all blend compositions, while the lower critical solution temperature exceeds thermal decomposition. Furthermore, as shown in Figure 3, the T_g 's obtained are significantly higher than the calculated ones based on the Flory-Fox equation,¹⁴ indicative of significant intermolecular interactions. In model studies, we have determined a K_{ass} of 10^2 using the ¹H-NMR titration technique,¹⁵ while Job plots¹⁶ unambiguously have shown 1:1 complexes for imides and 2,6-diaminopyridine derivatives.¹⁷

The supramolecular blends prepared are extremely brittle, and therefore, the determination of the ultimate mechanical properties is not feasible, unfortunately. In strong polar solvents, like DMSO, the blends are readily soluble, indicating that the blends are based on secondary interactions. The prominent role of cooperativity of the three hydrogen bonds in the blends of **1** and **3** is demonstrated with the blend of the *N*-methyl derivative¹⁸ of **1** with **3**. In all compositions studied, a phase-separated blend is observed with two glass transitions at 204 and 220 °C, which correspond to those of the individual components, *N*-methyl-**1** and **3**, respectively.

Conclusions. The characterization of all the blend compositions of **1** with **2** and **1** with **3**, as well as model studies show, that multiple-hydrogen bonding can give rise to high compatibility. Disturbing the specific interactions by introducing an *N*-methyl group in the polyimide leads to heterogeneous polymer blends, emphasizing the prominent role of the complementary couples. The polymer blends obtained, however, are all amorphous, without showing distinct topologies. Long range cooperativity is expected as soon as well-defined stereoregular polymers are used. Future research will be focused on material properties, chain-length dependence of the miscibility, and the supramolecular architecture with more stereoregular polymers.

Acknowledgment. The authors acknowledge the fruitful discussions with and experimental support of many colleagues at DSM Research. The group of Dr.

J. Kanters, University of Utrecht, is acknowledged for the X-ray analysis of the melamine complexes.

References and Notes

- (1) For some background in supramolecular chemistry, see: (a) Lehn, J.-M. *Angew. Chem.* **1988**, *100*, 91. (b) Cram, D. *Angew. Chem.* **1988**, *100*, 1041. (c) Feng, Q.; Park, T. K.; Rebek, J. *Science* **1992**, *256*, 1179. (d) Philp, D.; Stoddart, J. F. *Synlett* **1991**, 445. (e) Lindsey, J. *New J. Chem.* **1991**, *15*, 153. (f) Fan, E.; Yang, J.; Geib, S. J.; Vincent, C.; Garcia-Tellado, F.; Tecilla, P.; Hamilton, A. D. *Macromol. Symp.* **1994**, *77*, 209. (g) Whitesides, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312.
- (2) (a) Ringsdorf, H.; Schlarb, F.; Venzmer, G. *Angew. Chem.* **1988**, *100*, 117. (b) Percec, V.; Heck, J.; Johansson, G.; Tomazos, D.; Kawasumi, M.; Ungar, G. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 1031. (c) Wegner, G. *Mol. Cryst. Liq. Cryst.* **1993**, *235*, 1. (d) Gibson, H. W.; Marand, H.; *Adv. Mater.* **1993**, *5*, 11.
- (3) (a) Fouquey, C.; Lehn, J.-M.; Levelut, A.-M. *Adv. Mater.* **1990**, *2*, 254. (b) Kotera, M.; Lehn, J.-M.; Vigneron, J.-P. *J. Chem. Soc., Chem. Commun.* **1994**, 197. (c) Marsh, A.; Nolen, E. G.; Gardinier, K. M.; Lehn, J.-M. *Tetrahedron Lett.* **1994**, *35*, 397.
- (4) (a) Kato, T.; Kihara, H.; Uryu, T.; Fujishima, A.; Fréchet, J. M. J. *Macromolecules* **1992**, *25*, 6836. (b) Kato, T.; Kihara, H.; Kumar, U.; Fujishima, A.; Uryu, T.; Fréchet, J. M. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34* (2), 722. (c) Kumar, U.; Kato, T.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1992**, *114*, 6630.
- (5) (a) Hilger, C.; Dräger, M.; Stadler, R. *Macromolecules* **1992**, *25*, 2498. (b) Stadler, R.; Hellmann, J.; Schirle, M.; Beckmann, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34* (2), 100. (c) Hilger, C.; Stadler, R.; *Macromolecules* **1992**, *25*, 6670. (d) Abetz, V.; Hilger, C.; Stadler, R. *Makromol. Chem. Makromol. Symp.* **1991**, *52*, 131.
- (6) (a) Rodriguez-Parada, J. M.; Percec, V. *Macromolecules* **1986**, *19*, 55. (b) Pugh, C.; Percec, V. *Macromolecules* **1986**, *19*, 65. (c) Rodriguez-Parada, J. M.; Percec, V. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 579. (d) Pugh, C.; Rodriguez-Parada, J. M.; Percec, V. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 747. (e) Percec, V.; Schild, H. G.; Rodriguez-Parada, J. M.; Pugh, C. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 935.
- (7) Eisenberg, A.; Hara, J. *Polym. Eng. Sci.* **1984**, *22*, 307.
- (8) (a) Coleman, M. M.; Graf, J. F.; Painter, P. C. *Specific Interactions and the Miscibility of Polymer Blends*, Technomic Publishers Inc.: Lancaster, PA, 1991. (b) Pearce, E. M.; Kwei, T. K.; Min, B. Y. *J. Macromol. Sci., Chem. A* **1984**, *21*, 1121. (c) Kwei, T. K. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 307.
- (9) van Paesschen, G.; Timmerman, D. *Makromol. Chem.* **1964**, *78*, 112.
- (10) Yuki, Y.; Kakurai, T.; Noguchi, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2123.
- (11) No reflections at 3.19 and 3.26 Å for condensated melamine products could be determined.
- (12) Extrapolation of the X-ray reflection data at 3.41 Å for the blend yields a value of zero at a mixture with 19.7 weight % melamine and 80.3 weight % of polymer **1**. This ratio corresponds with a molar ratio of 2.6:1 for 1:2. Full complementarity is possible at a ratio of 3:1.
- (13) (a) Zerkowski, J. A.; MacDonald, J. C.; Seto, C. T.; Wierda, D. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 2382. (b) Zerkowski, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 4298. (c) Zerkowski, J. A.; Mathias, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 4305. (d) Mathias, J. P.; Simanek, E. E.; Zerkowski, J. A.; Seto, C. T.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 4316. (e) Mathias, J. P.; Simanek, E. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 4326.
- (14) Fox, T. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.
- (15) Foster, R.; Fyfe, C. *Organic Charge-Transfer Complexes*; Academic Press: London and New York, 1969.
- (16) Vosburgh, W.; Cooper, G. *J. Am. Chem. Soc.* **1941**, *63*, 437.
- (17) For solubility reasons the structurally related 2,6-(diacetyl-amino)pyridine and other diacetylated 2,6-diaminopyridines are used. For more information on the supramolecular interactions of 2,6-(diacetyl-amino)pyridines and imides see: Hamilton, A. D.; Van Engen, D. *J. Am. Chem. Soc.* **1987**, *109*, 5035.
- (18) Winter, H.; van der Velden, G. *Macromolecules* **1992**, *25*, 4285.