Polymer Vol. 37 No. 10, pp. 1841–1845, 1996
Published by Elsevier Science Ltd
Printed in Great Britain.
0032-3861/96/$15.00 + 0.00

Molecular dynamics simulation of a single-component molecular composite: poly(*p*-phenylene benzobisthiazole)/*meta*-poly(aryl ether ketone) block copolymer

Steven Trohalaki
Wright Laboratory/MLPJ, Building 651, 3005 P Street, Suite 1, Wright-Patterson Air Force Base, OH 45433-7702, USA

(Received 21 July 1995)

Molecular dynamics simulations were performed with a model of a single-component molecular composite in the form of a block copolymer composed of poly(*p*-phenylene benzobisthiazole) rigid-rod and flexible *meta*-poly(aryl ether ketone) subunits. The molecular composite concept, applied to improve the compressive strength of rigid-rod polymers and to improve their solubility, relies on a uniform distribution of rods in a coil-like matrix. Pair distribution functions, orientation correlation functions and correlation volumes calculated from equilibrium dynamics trajectories of bulk copolymer, coil homopolymer and rigid-rod homopolymer systems imply that, while inter-rod spacing is only slightly increased in the copolymer, correlation of rod orientation is greatly reduced but to a somewhat lesser extent than previously found for a graft copolymer composed of identical subunits. Conformations of the flexible blocks extend to accommodate the partial rod alignment. The block copolymer topology appears to be a viable alternative to the hairy-rod graft copolymer as a single-component molecular composite. Published by Elsevier Science Ltd.

(Keywords: molecular dynamics simulations; molecular composites; rigid-rod polymers)

INTRODUCTION

Poly(*p*-phenylene benzobisthiazole) (PBZT; see *Figure 1*) belongs to a class of rigid-rod aromatic heterocyclic polymers that, when processed into fibres or films, exhibit such beneficial properties as thermo-oxidative resistance, environmental stability and excellent mechanical characteristics. These properties are due to both the inherent molecular modulus and the degree of molecular orientation[1–3]. However, PBZT fibres have been found to have low compressive strength compared to poly(acrylonitrile)-based carbon fibres[4–7]. Also, processing into bulk forms, required for structural applications, is hampered by solubility limited to strong acids such as methanesulfonic acid and polyphosphoric acid, because PBZT degrades before it melts.

The concept of molecular composites[8–13] has been explored to circumvent the problems associated with processing as well as to improve compressive strength. Originally, the concept consisted of blending a rigid-rod aromatic heterocyclic polymer with a coil-like aromatic heterocyclic polymer with the intention of reinforcing the amorphous matrix of coils with rigid rods. The composite, formed on a molecular level, relies on a uniform distribution of individual rod-like polymers throughout the coil-like polymer matrix. The composite would therefore not suffer from the interfacial adhesion problems or thermally induced macroscopic stresses (caused by differences in thermal expansion coefficients) inherent in a macroscopic composite, such as a chopped glass-fibre reinforced epoxy.

However, the incompatability over nearly a full range of concentration between rods and coils due to an unfavourable entropy of mixing was shown by Flory[14] for ternary systems of solvent, rods and coils. Painter *et al.*[15], though, have reported a thermodynamically stable dispersion of rigid-rod poly(L-glutamates) in a poly(4-vinylphenol) random-coil matrix; the favourable free energy resulting from hydrogen bonding apparently balances the unfavourable entropy of mixing.

Extending the theory of Flory, Ballauff[16] showed that miscibility over a wider range of composition results from appending flexible side chains to the rods. Such a single-component molecular composite should show improvements in fracture and impact toughness as well as in dimensional stability because translation of stress or strain from the reinforcing rigid-rod will be more efficient as a consequence of it being chemically bonded to the matrix.

Several workers have explored the single-component molecular composite suggested by Ballauff, in which flexible side chains are grafted onto a rigid-rod polymer, referred to as combs or hairy rods. Heitz *et al.*[17] found

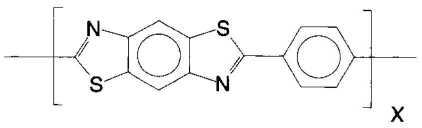

Figure 1 Repeat unit for poly(*p*-phenylene benzobisthiazole) (PBZT)

that liquid-crystalline polyesters with polystyrene side chains showed improved miscibility with polystyrene. The graft copolymer formed a three-dimensional network that penetrated the polystyrene matrix. Wegner and coworkers[18,19] reported that rod-like copoly(methyl/hexadecyl-L-glutamate) decorated with hydrocarbon side chains self-organizes into monolayers of nematic texture.

Previously, molecular dynamics simulations of bulk systems of hairy-rod molecular composites and of unsubstituted rods were performed[20]. Hairy rods were modelled as PBZT trimers each with a pendent *meta*-poly(aryl ether ketone) (*m*PEK, a tough, thermally stable thermoplastic; see *Figure 2*) trimer. Unsubstituted rods were modelled as PBZT trimers. Analysis and comparison of the dynamics trajectories imply that the presence of pendent *m*PEK does not appear to alter the spacing of the rods although correlation of rod orientation is greatly reduced. Both observations are congruous with the molecular composite concept—a uniform distribution of rods throughout the amorphous matrix.

Synthesis[21], processing[22] and morphology[23] of hairy-rod systems have been presented previously. Improvement in solubility was observed for the graft copolymer, which is soluble in trifluoroacetic acid, whereas PBZT homopolymer is soluble only in methanesulfonic acid and polyphosphoric acid. Thermal stability is only slightly lower for hairy rods, with substantial breakdown in air occurring in the range of 430–450°C[21]. Softening temperatures were found to be in the range of 180–265°C[21]. Softening and improved processibility was determined to be due to secondary relaxation of the *m*PEK chains[22]. X-ray analysis showed rod aggregation, but it is believed that this occurs between portions of the rod with very low frequency of graft sites[23]. The graft copolymers exhibited stability against thermally induced aggregation, implying that this topology is an effective approach in preventing rod aggregation during thermal processing[23].

Tsai *et al.*[24] found that block copolymers composed of PBZT rod and benzimidazole coil blocks display enhanced tensile properties. Here, a PBZT/*m*PEK block copolymer, a topological alternative to the hairy-rod molecular composite, is considered. Analysis of the spatial properties of the bulk copolymer and comparison to those of the rod and coil homopolymers will suggest whether or not this distribution is realized experimentally.

MODELS AND SIMULATION METHOD

Molecular dynamics simulations employed cubic periodic boundary conditions with the minimum-image convention. The united-atom approximation was used, i.e. hydrogens were not explicitly considered. The CHARMm force field, as implemented by the QUANTA molecular modelling software package (Molecular Simulations Inc., Burlington, MA), was employed. Integration of Newton's equations of motion was performed with the Verlet method[25]. Non-bond neighbour lists were updated every 15 integrations. The dielectric constant was made proportional to the atomic pair separation; this option in CHARMm approximates solvent screening and was deemed appropriate for simulations of polymer structures in the absence of explicit solvent molecules. The periodic structures were minimized prior to dynamics simulation to alleviate any unfavourable contacts. Molecular dynamics simulations of bulk systems were performed for 150 ps or longer after equilibrium was established. All simulations were performed at 300 K.

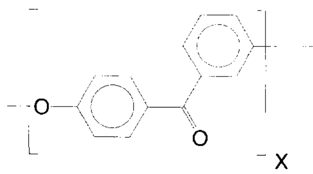

Figure 2 Repeat unit for *meta*-poly(aryl ether ketone) (*m*PEK)

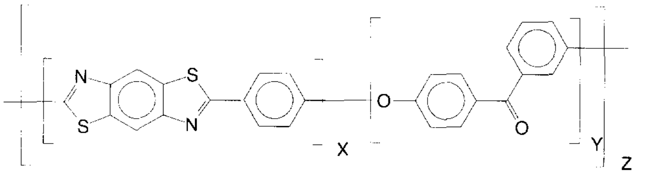

Figure 3 Repeat unit for the copolymer simulated in this work; $X = 2$, $Y = 7$, $Z = 21$

The block copolymer simulated here consists of a PBZT dimer attached to an *m*PEK heptamer. The degree of polymerization for the repeat unit is 20, i.e. X, Y and Z in *Figure 3* have the values 2, 7 and 20, respectively (except that, for convenience in building the polymer, a single *m*PEK repeat unit is attached to the initial PBZT block and the last *m*PEK block consists of only four repeat units), for a total of 2805 atoms.

The dimension of the periodic box was chosen to be 1.5 times the extended length of the rod portion of the molecule, 39.8 Å, corresponding to a density of $1.0\,\mathrm{g\,cm^{-3}}$. Using a periodic box of the same dimension, *m*PEK homopolymer was modelled as a chain with degree of polymerization equal to 162, also corresponding to a density of $1.0\,\mathrm{g\,cm^{-3}}$, for a total of 2431 atoms. The control simulation for PBZT homopolymer is the same as that used in the previous study of hairy rods[20], where unsubstituted PBZT trimers were simulated at a lower density, $0.5\,\mathrm{g\,cm^{-3}}$. It is assumed that rod orientation and packing of this system approximates that of a $1\,\mathrm{g\,cm^{-3}}$ system of dimers; while packing to a lesser degree can be expected from a less dense system, higher orientation should result from the larger aspect ratio.

RESULTS

The initial configuration of the block copolymer was a roughly spherical random coil, which did not substantially change during minimization. Dynamics equilibration, however, resulted in an elongated spatial arrangement, as seen in *Figure 4*. In contrast, the *m*PEK configuration started out and remained a roughly spherical, random coil. Equilibration of the system of unsubstituted PBZT rods, initially randomly oriented, resulted in a large degree of rod alignment[20]. These observations are quantified below.

Local orientation is often represented as the orientation-correlation function, $S(r)$:

$$S(r) = 0.5(3\langle\cos^2\phi_{ij}\rangle - 1) \qquad (1)$$

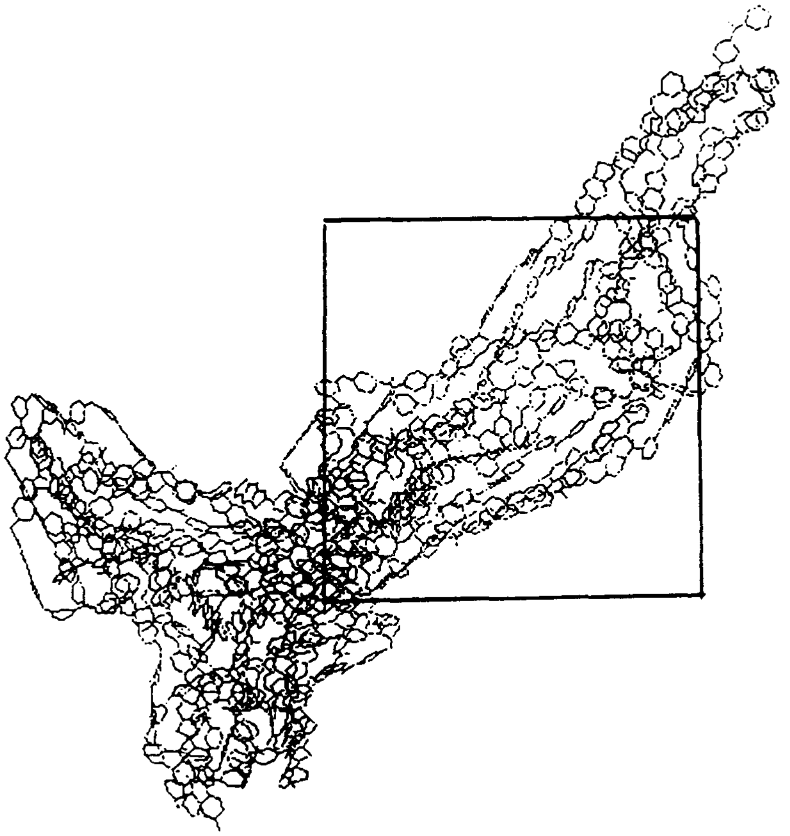

Figure 4 A typical single frame of the parent chain taken from the equilibrium dynamics trajectory of the PBZT/*m*PEK block copolymer. Periodicity is not displayed

where ϕ_{ij} is the angle between two vectors i and j whose midpoints are separated by a distance r. The function $S(r)$ was calculated for the end-to-end vectors of PBZT blocks and *m*PEK blocks in the copolymer, for end-to-end vectors of *m*PEK heptamer blocks in the *m*PEK homopolymer, and for end-to-end vectors of PBZT rods in the PBZT trimers. The midpoints of these vectors were used to calculate the pair distribution function, $g(r)$, and the correlation volume, V_ξ:

$$V_\xi = 4\pi \int_0^\infty r^2 S(r) g(r)\, \mathrm{d}r \qquad (2)$$

a measure of the volume in which local orientations are correlated.

A plot of $S(r)$ weighted by $g(r)$ is shown as a function of r for end-to-end vectors representing PBZT blocks in the copolymer in *Figure 5a*, where it is seen that a maximum in orientation correlation occurs at a spacing of about 5 Å. *Figure 5b* shows that the maximum in $S(r)g(r)$ occurs at 4 Å for the bulk PBZT system. In the case of the *m*PEK blocks in the copolymer, maximum orientation correlation occurs at a separation of about 2–3 Å (see *Figure 6a*) as compared to 1–2 Å for heptamer blocks in the *m*PEK homopolymer (see *Figure 6b*).

V_ξ calculated for rod blocks in the copolymer, 11 900 Å^3, is almost identical to those for the coil blocks, 12 000 Å^3, as must be the case because each set of vectors connects to the endpoints of the other. In the copolymer, the rod correlation volume, equivalent to the volume of a sphere with a radius of 14 Å, is only one-thirtieth of that for a bulk system of PBZT rods, 357 000 Å^3, equivalent to the volume of a sphere of

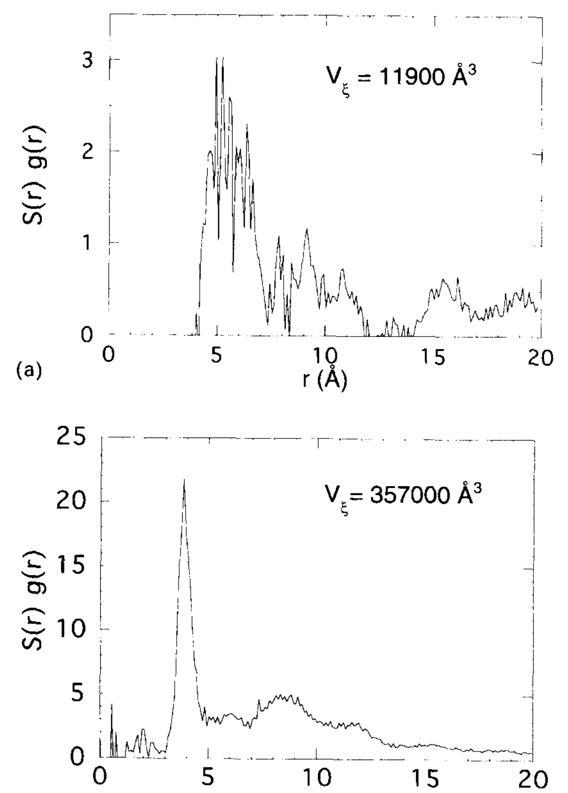

Figure 5 The orientation correlation function weighted by the pair distribution function plotted as a function of separation for end-to-end vectors representing (a) PBZT rod blocks in the bulk copolymer system, and (b) rods in the bulk system of PBZT trimers

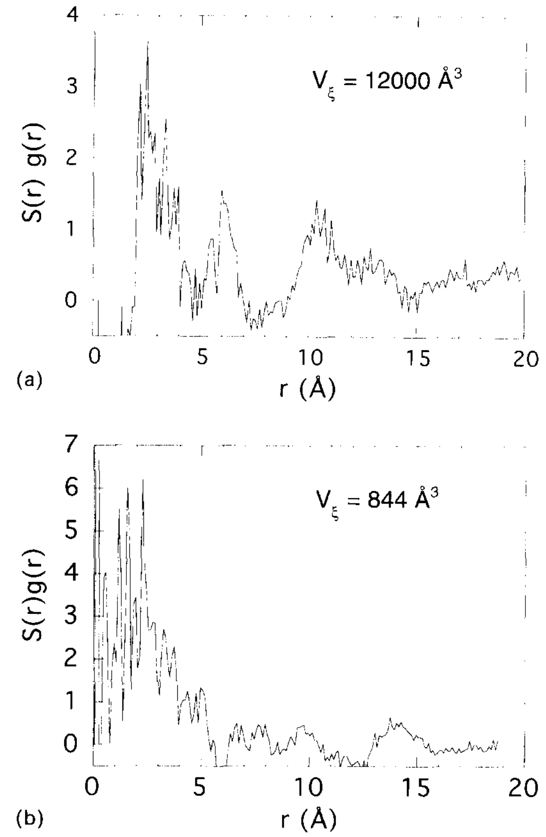

Figure 6 The orientation correlation function weighted by the pair distribution function plotted as a function of separation for end-to-end vectors representing (a) *m*PEK blocks in the bulk copolymer system, and (b) heptamers in the bulk *m*PEK homopolymer system

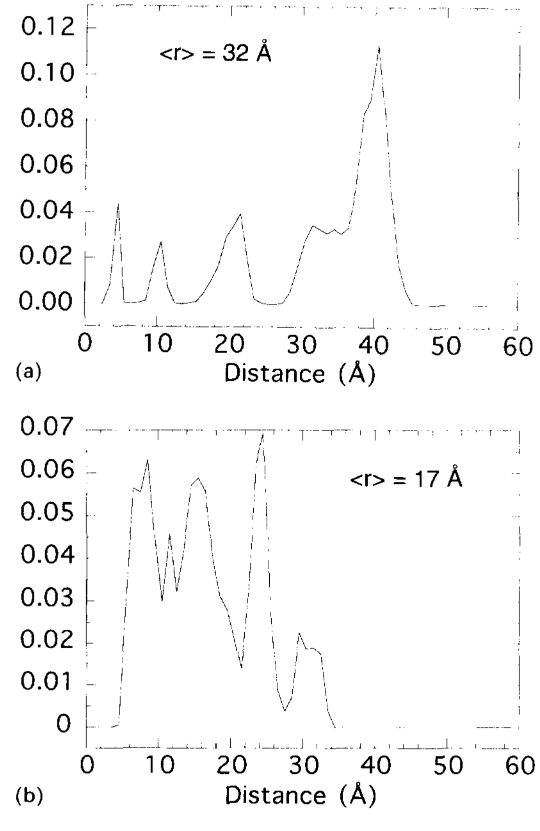

Figure 7 End-to-end length distribution for (a) *m*PEK blocks in the bulk copolymer system, and (b) heptamers in the bulk *m*PEK homopolymer system

radius 44 Å. V_ξ for the rods in the copolymer is about twice that found previously for the hairy-rod molecular composite simulated at half the density.

Just as the orientation correlation for PBZT rods decreases as a result of incorporation into the copolymer, a concomitant increase is seen for the *m*PEK coils. V_ξ for the end-to-end vectors of heptamer blocks in the *m*PEK homopolymer is 844 Å^3 (equivalent to a sphere of about 6 Å radius), over an order of magnitude lower than that for vectors representing *m*PEK blocks in the copolymer. Comparison of the end-to-end distributions for copolymer coil blocks and *m*PEK homopolymer heptamers, displayed in *Figures 7a* and *7b*, respectively, shows that *m*PEK adopts a much more extended configuration as a consequence of incorporation into the copolymer. The orientation of this extension is significantly correlated, as noted above. The average end-to-end distance for *m*PEK blocks in the copolymer, 32 Å (standard deviation = 11 Å), is about twice that of heptamers in the homopolymer, 17 Å (standard deviation = 7 Å). The flexibility of the *m*PEK blocks accommodates the partial alignment of the PBZT blocks.

CONCLUSIONS

Placing PBZT rods in a matrix of *m*PEK via a block-copolymer topology greatly reduces correlation of rod orientation while only slightly increasing the average spacing. Still, a significant degree of order persists. Rods in the block copolymer display a correlation volume about twice that in the graft copolymer. This comparison is somewhat tenuous due to the discrepancy in the densities of the two systems. A better indication of the order is the observation that correlation volume for end-to-end vectors of *m*PEK heptamers is an order of magnitude larger in the copolymer than for heptamer blocks in the *m*PEK homopolymer.

PBZT rods effectively extend the *m*PEK block configurations in the copolymer by a factor of about 2. The orientation of this extension is moderately correlated and is consistent with the elongated shape of the copolymer chain.

The block-copolymer topology appears to be a viable alternative to the hairy-rod graft copolymer as a single-component molecular composite. Future work, including variation of the block lengths, will make this conclusion more definite. Prediction of the bulk modulus of these systems will investigate the effect of these spatial arrangements of rods in a coil matrix and the potential of molecular composites as bulk materials.

ACKNOWLEDGEMENT

It is a pleasure to acknowledge the Polymer Branch of the Materials Directorate at Wright Laboratory, where this project originated, for the computer resources used for this work.

REFERENCES

1 Helminiak, T. E. *Prepr. ACS Div. Org. Coat. Plast.* 1979, **40**, 475
2 Wolf, J. F., Loo, B. H. and Arnold, F. E. *Macromolecules* 1981, **14**, 915
3 Cohen, Y. and Thomas, E. L., *Macromolecules* 1988, **21**, 433, 436
4 Adams, W. W. and Eby, R. K. *Mater. Res. Soc. Bull.* 1987, **12**, 22

5 Ulruch, D. R. *Polymer* 1987, **28**, 533

6 Allen, S. R., Filippov, A. G., Farris, R. J., Thomas, E. L., Wong, C.-P., Berry, G. C. and Chenevey, E. C. *Macromolecules* 1981, **14**, 1135

7 Kumar, S. and Helminiak, T. E. Mater. Res. Soc. Meeting, Fall 1988, Abstr., p. 307

8 Helminiak, T. E. *et al.*, US Pat. 4207407, 1980

9 Wellman, M., Husman, G., G. Kulshreshtha, G., Helminiak, T., Wiff, D., Benner, C. and Hwang, W. F. *ACS Div. Org. Coat. Plast. Chem. Prepr.* 1980, **43**, 783

10 Hwang, W., F., Wiff, D. R. and Helminiak, T. E. *ACS Div. Org. Coat. Plast. Chem.* 1980, **44**, 32

11 Hwang, W. F. Wiff, D. R., Benner, C. and Helminiak, T. E. *J. Macromol. Sci. (B)* 1983, **22**, 231

12 Hwang, W. F., Wiff, D. R, Verschoore, C., Price, G. E., Helminiak, T. E. and Adams, W. W. *Polym. Eng. Sci.* 1983, **23**, 784

13 Krause, S. J., Haddock, T., Price, G. E., Henhert, P. G., O'Brien, J. F., Helminiak, T. E. and Adams, W. W. *J. Polym. Sci. (B) Polym. Phys.* 1986, **24**, 1991

14 Flory, P. J. *Macromolecules* 1978, **11**, 1138

15 Painter, P. C., Tang, W.-L., Graf, J. F., Thomson, B. and Coleman, M. M. *Macromolecules* 1991, **24**, 3929

16 Ballauff, M. *J. Polym. Sci. (B) Polym. Phys.* 19987, **25**, 739

17 Heitz, T., Rohrback, P. and Hocker, H. *Makromol. Chem.* 1989, **190**, 3295

18 Bubek, C., Duda, G., Grund, A., Hickel, W., Kaltbeitzel, A., Mathy, A., Meyer, W. A., Neher, D., Saur, T., Simmrock, H.-U., Wegner, G., Wolf, A. and Knoll, W. *Polym. Prepr.* 1991, **323**, 69

19 Wegner, G. *Makromol. Chem., Macromol. Symp.* 1991, **48/49**, 419

20 Trohalaki, S. and Dudis, D. S. *Makromol. Chem., Macromol. Symp.* 1993, **65**, 163

21 Dotrong, M. H., Dotrong, H. and Evers, R. C. *Polym. Prepr.* 1992, **331**, 477

22 Vakil, U., Wang, C.-S., Lee, C., Dotrong, M. H., Dotrong, M. and Evers, R. C. *Polym. Prepr.* 1992, **331**, 479

23 Song, H. H., Price, G. E., Vakil, U. and Dotrong, M. H. *Polym. Prepr.* 1992, **331**, 319

24 Tsai, T. T., Arnold, F. E. and Hwang, W. F. *Polym. Prepr.* 1985, **261**, 144

25 Verlet, L. *Phys. Rev.* 1967, **159**, 98