Polymer Solutions: An Introduction to Physical Properties. Iwao Teraoka
Copyright © 2002 John Wiley & Sons, Inc.
ISBNs: 0-471-38929-3 (Hardback); 0-471-22451-0 (Electronic)

REFERENCES

1. M. Doi, *Introduction to Polymer Physics*, Oxford Univ. Press: Clarendon, 1996.
2. J. des Cloizeaux, G. Jannink, *Polymers in Solution: Their Modelling and Structure*, Oxford Univ. Press: Clarendon (1990).
3. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca (1953).
4. S. Trainoff, P. J. Wyatt, in *International GPC Symposium '98.* R. Nielson, Ed. Waters: Milford (1999).
5. Y. Wang, I. Teraoka, *Macromolecules* **33**, 3478 (2000).
6. P. Cifra, T. Bleha, *Macromol Theory Simul* **8**, 603 (1999).
7. M. M. Green, N. C. Peterson, T. Sato, A. Teramoto, R. Cook, *Science* **268**, 1860 (1995).
8. H. Murakami, T. Norisuye, H. Fujita, *Macromolucules* **13**, 345 (1980).
9. P. M. Cotts, Z. Guan, E. McCord, S. McLain, *Macromolucules* **33**, 6945 (2000).
10. S. Matsuyama, H. Nakahara, K. Takeuchi, R. Nagahata, S. Kinugasa, I. Teraoka, *Polym J* **32**, 249 (2000).
11. J. Brandrup, E. H. Immergut, E. A Grulke, Ed. *Polymer Handbook* (4th Ed), Wiley: New York (1999).
12. M. L. Huggins, *Ann. NY Acad Sci* **43**, 1 (1942).
13. E. A. Guggenheim, *Mixtures*, Oxford University Press: London, 1952.
14. J. P. Cotton, *J Phys Lett* **41**, L-231 (1980).
15. A. R. Shultz, P. J. Flory, *J Am Chem Soc* **74**, 4760 (1952).
16. C. Strazielle, H. Benoit, *Macromolucules* **8**, 203 (1975).
17. A. Z. Panagiotopoulos, V. Wong, M. A. Floriano, *Macromolecules* **31**, 912 (1998).
18. P. Grassberger, R. Hegger, *J Chem Phys* **102**, 6881 (1995).
19. X. Wang, X. Qiu, C. Wu. *Macromolecules* **31**, 2972 (1998).
20. Y. Wang, Private communications.
21. B. Chu, *Laser Light Scattering: Basic Principles and Practice* (2nd ed.), Academic Press: San Diego, 1991.
22. K. S. Schmitz, *An Introduction to Dynamic Light Scattering by Macromolecules*, Academic Press: San Diego, 1990.
23. M.-P. Nieh, A. A. Goodwin, J. R. Stewart, B. M. Novak, D. A. Hoagland, *Macromolecules* **31**, 3151 (1998).
24. Waters, Inc.
25. Wyatt Technology Corporation.
26. D. Pötschke, M. Ballauff, P. Lindner, M. Fischer, F. Vögtle, *Macromolecules* **32**, 4079 (1999).
27. E. F. Casassa, *J Polym Sci Polym Lett Ed.* **5**, 773 (1967); E. F. Casassa, Y. Tagami, *Macromolecules* **2**, 14 (1969),
28. J. C. Giddings, E. Kucera, C. P. Russell, M. N. Myers, *J Phys Chem* **72**, 4397 (1968).
29. I. Teraoka, *Progr. Polym Sci* **21**, 89 (1996).
30. M. T. Bishop, K. H. Langley, F. E. Karasz, *Macromolecules* **22**, 1220 (1989).
31. I. Suda, Y. Tominaga, M. Osa, T. Yoshizaki, H. Yamakawa, *Macromolecules* **33**, 9322 (2000).
32. S. W. Provencher, *Macromol Chem* **180**, 201 (1979).

33. K. H. Langley, I. Teraoka, in *Methods in the Physics of Porous Media*. P.-Z. Wong, Ed. Academic Press: San Diego (1999).
34. D. S. Viswanath, G. Natarajan, *Data Book on the Viscosity of Liquids*, Hemisphere, New York (1989).
35. R. Balic, R. G. Gilbert, M. D. Zammit, T. P. Davis, C. M. Miller, *Macromolecules* **30**, 3775 (1997).
36. P. E. Rouse, *J Chem Phys* **21**, 1272 (1953).
37. B. H. Zimm, *J Chem Phys* **24**, 269 (1956).
38. Y. Oono, M. Kohmoto, *J Chem Phys* **78**, 520 (1983).
39. C. Kuo, T. Provder, R. A. Sanayei, K. F. O'Driscoll in *International GPC Symposium '94*. R. Nielson, Ed. Waters, Milford (1994).
40. D. W. Schaefer, C. C. Han, in *Dynamic Light Scattering*. Ed. R. Pecora, Plenum, NY (1985).
41. J. G. Kirkwood, P. L. Auer, *J Chem Phys* **19**, 281 (1951).
42. H. Yamakawa, *Helical Wormlike Chains in Polymer Solutions*, Springer, Berlin (1997).
43. T. Itou, H. Chikiri, A. Teramoto, S. M. Aharoni, *Polym J* **20**, 143 (1988).
44. P.-G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell Univ. Press: Ithaca (1979).
45. M. Doi, S. F. Edwards, *The Theory of Polymer Dynamics*, Oxford Univ. Press: Clarendon (1986).
46. I. Noda, N. Kato, T. Kitano, M. Nagasawa, *Macromolecules* **14**, 668 (1981).
47. T. Ohta, Y. Oono, *Phys Lett* **89A**, 460 (1982).
48. P. Wiltzius, H. R. Haller, D. S. Cannell, D. W. Schaefer, *Phys Rev Lett* **51**, 1183 (1983).
49. M. Daoud, J. P. Cotton, B. Farnoux, G. Jannink, G. Sarma, H. Benoit, R. Duplessix, C. Picot, P.-G. de Gennes. *Macromolecules* **8**, 804 (1975).
50. Y. Oono, *Adv Chem Phys* **61**, 301 (1985).
51. W. Brown, T. Nicolai, in *Dynamic Light Scattering: The Method and Some Applications.* Ed. W. Brown, Oxford Univ. Press: Clarendon (1993).
52. L. Léger, H. Hervet, F. Rondelez, *Macromolecules* **14**, 1732 (1981).
53. L. M. Wheeler, T. P. Lodge, *Macromolecules* **22**, 3399 (1989).
54. N. A. Rotstein, T. P. Lodge, *Macromolecules* **25**, 1316 (1992).

FURTHER READINGS

There are several textbooks and research monographs on polymer solutions. Some of the contents partly overlap with the scope of this textbook. The following books are recommended to readers interested in further studies:

1. P.-G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell Univ. Press: Ithaca (1979).

   This is a good introduction to the scaling theory by the pioneer of the theory. The scaling concept is used for polymer solutions, polymer blends, melts, and gels.

2. M. Doi, S. F. Edwards, *The Theory of Polymer Dynamics*, Oxford Univ. Press: Clarendon (1986).

   Detailed explanations on theoretical tools are given. Emphasis is on viscoelastic properties. The book contains a few chapters on dilute, semidilute, and concentrated solutions of rodlike molecules. The following is a simplified version: M. Doi, *Introduction to Polymer Physics*, Oxfor Univ. Press: Clarendon, 1996.

3. G. Strobl, *The Physics of Polymers* (2nd ed), Springer: Berlin (1997).

   This book deals with polymer physics in general, including solid states of polymers. It offers a succinct account of solution properties.

4. H. Yamakawa, *Helical Wormlike Chains in Polymer Solutions*, Springer: Berlin (1997).

   This book offers a detailed explanation on conformation and dynamics of wormlike chains and helical wormlike chains by an expert of the model.

5. H. Morawetz, *Macromolecules in Solution* (2nd ed), Wiley: New York (1975).

   This book is a historical standard of polymer solution textbook. It is now available from Krieger.

6. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press: Ithaca, 1953.

   This book is another historical standard of polymer in general.

7. A. Y. Grosberg, A. R. Khokhlov, *Statistical Physics of Macromolecules*, AIP Press: Woodbury, 1994.

   This book offers a detailed account of the scaling theory. It contains many applications.

8. J. des Cloizeaux, G. Jannink, *Polymers in Solution: Their Modelling and Structure*, Oxford Univ. Press: Clarendon (1990).

   This book offers a detailed account of the renormalization group theory. The book contains an excellent review of many experimental data on the thermodynamic properties of polymer solutions.

9. H. Fujita, *Polymer Solutions*, Elsevier: Amsterdam (1990).

   This book offers a formal introduction to polymer solution theory. It contains many experimental data.

There are several books on light scattering:

1. K. S. Schmitz, *An Introduction to Dynamic Light Scattering by Macromolecules*, Academic Press: San Diego, 1990.
2. B. Chu, *Laser Light Scattering: Basic Principles and Practice* (2nd ed.), Academic Press: San Diego, 1991.
3. W. Brown ed. *Dynamic Light Scattering: The Method and Some Applications*, Oxford Univ. Press: Clarendon, 1993.

Polymer Solutions: An Introduction to Physical Properties. Iwao Teraoka

ISBNs: 0-471-38929-3 (Hardback); 0-471-22451-0 (Electronic)

APPENDIX

Some of the mathematics used in this textbook are detailed here.

A1 DELTA FUNCTION

A delta function [$\delta(x)$] has an infinite value at $x = 0$ and is zero everywhere else. It is impossible to draw a plot of $\delta(x)$, but it may be convenient to regard it as a positive spike at $x = 0$. The integral of $\delta(x)$ over a finite interval that contains $x = 0$ is 1:

$$\int_{0^-}^{0^+} \delta(x)\,\mathrm{d}x = \boxed{\int_{-\infty}^{\infty} \delta(x)\,\mathrm{d}x = 1} \qquad \text{(A1.1)}$$

where 0^- is infinitesimally smaler than 0, and 0^+ is infinitesimally greater than 0. On integration of the product of $\delta(x)$ and an arbitrary function $f(x)$, we obtain

$$\boxed{\int_{-\infty}^{\infty} \delta(x) f(x)\,\mathrm{d}x = f(0)} \qquad \text{(A1.2)}$$

The following formula is useful:

$$\boxed{\int_{-\infty}^{\infty} \delta(x-a) f(x)\,\mathrm{d}x = f(a)} \qquad \text{(A1.3)}$$

In three dimensions, we write

$$\delta(\mathbf{r}) \equiv \delta(x)\delta(y)\delta(z) \qquad \text{(A1.4)}$$

It is easy to find

$$\boxed{\int_{-\infty}^{\infty} \delta(\mathbf{r})\,\mathrm{d}\mathbf{r} = 1} \qquad \text{(A1.5)}$$

where $\mathrm{d}\mathbf{r} = \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$ and the range of integration can be any volume that contains $\mathbf{r} = 0$. We can evaluate an arbitrary function $f(\mathbf{r})$ at $\mathbf{r} = \mathbf{a}$:

$$\boxed{\int_{-\infty}^{\infty} \delta(\mathbf{r}-\mathbf{a}) f(\mathbf{r})\,\mathrm{d}x = f(\mathbf{a})} \qquad \text{(A1.6)}$$

There are several ways to define $\delta(x)$ by an equation. One of them is

$$\boxed{\delta(x) \equiv \frac{1}{2\pi}\int_{-\infty}^{\infty} \exp(\mathrm{i}kx)\,\mathrm{d}k} \tag{A1.7}$$

In three dimensions,

$$\boxed{\delta(\mathbf{r}) \equiv \frac{1}{(2\pi)^3}\int_{-\infty}^{\infty} \exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r})\,\mathrm{d}\mathbf{k}} \tag{A1.8}$$

A2 FOURIER TRANSFORM

For an arbitrary function $f(x)$ of a space variable x, its Fourier transform $\hat{f}(k)$ is defined by

$$\hat{f}(k) \equiv \int_{-\infty}^{\infty} f(x)\exp(\mathrm{i}kx)\mathrm{d}x \tag{A2.1}$$

The variable k is called a wave vector also for one dimension. To see what information of $f(x)$ is carried into $\hat{f}(k)$, let us consider a sinusoidal wave with wave vector k_1 and amplitude A_1:

$$f(k) = A_1 \cos k_1 x = (A_1/2)[\exp(\mathrm{i}k_1 x) + \exp(-\mathrm{i}k_1 x)] \tag{A2.2}$$

Then, from the definition,

$$\begin{aligned}\hat{f}(k) &\equiv \frac{A_1}{2}\int_{-\infty}^{\infty}[\exp(\mathrm{i}k_1 x) + \exp(-\mathrm{i}k_1 x)]\exp(\mathrm{i}kx)\mathrm{d}x \\ &= \frac{A_1}{2}\int_{-\infty}^{\infty}[\exp(\mathrm{i}(k + k_1)x) + \exp(\mathrm{i}(k - k_1)x)]\mathrm{d}x \\ &= \pi A_1[\delta(k + k_1) + \delta(k - k_1)]\end{aligned} \tag{A2.3}$$

which means that $\hat{f}(k)$ is nonzero only at $k = \pm k_1$. The integral of $\hat{f}(k)$ in a range including $k = k_1$ or $k = -k_1$ but not both of them gives πA_1 that is proportional to the amplitude of the wave. $\hat{f}(k)$ indicates which wave-vector components are contained in $f(x)$.

Let us integrate $\hat{f}(k)\exp(-\mathrm{i}kx)$ with respect to k:

$$\int_{-\infty}^{\infty}\hat{f}(k)\exp(-\mathrm{i}kx)\mathrm{d}k = \int_{-\infty}^{\infty}\exp(-\mathrm{i}kx)\mathrm{d}k\int_{-\infty}^{\infty}f(x')\exp(\mathrm{i}kx')\mathrm{d}x'$$

$$= \int_{-\infty}^{\infty} f(x')\mathrm{d}x'\int_{-\infty}^{\infty}\exp[\mathrm{i}k(x'-x)]\mathrm{d}k \tag{A2.4}$$

$$= \int_{-\infty}^{\infty} f(x')\mathrm{d}x' 2\pi\delta(x'-x) = 2\pi f(x)$$

Thus, we can recover $f(x)$ from $\hat{f}(k)$ by

$$\boxed{f(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\hat{f}(k)\exp(-\mathrm{i}kx)\,\mathrm{d}k} \tag{A2.5}$$

This operation is called the inverse Fourier transform.

In three dimensions, the Fourier transform of a spatial function $f(\mathbf{r})$ is defined by

$$\hat{f}(\mathbf{k}) \equiv \int_{-\infty}^{\infty} f(\mathbf{r})\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r})\,\mathrm{d}\mathbf{r} \tag{A2.6}$$

The inverse transform is given by

$$f(\mathbf{r}) \equiv \frac{1}{(2\pi)^3}\int_{-\infty}^{\infty}\hat{f}(\mathbf{k})\exp(-\mathrm{i}\mathbf{k}\cdot\mathbf{r})\,\mathrm{d}\mathbf{k} \tag{A2.7}$$

We often need to calculate a three-dimensional Fourier transform of $f(r)$ that depends only on the radial distance r. For this purpose, we use a spherical polar coordinate for $\mathbf{r}$ with the polar axis running along $\mathbf{k}$. Then, the transform proceeds as follows.

$$\int f(r)\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r})\,\mathrm{d}\mathbf{r} = 2\pi\int_0^{\infty} r^2 f(r)\,\mathrm{d}r\int_0^{\pi}\sin\theta\exp(\mathrm{i}kr\cos\theta)\,\mathrm{d}\theta \tag{A2.8}$$

$$= \frac{4\pi}{k}\int_0^{\infty} rf(r)\sin kr\,\mathrm{d}r = \frac{4\pi}{k}\mathrm{Im}\int_0^{\infty} rf(r)\exp(\mathrm{i}kr)\,\mathrm{d}r$$

A3 INTEGRALS

Gaussian integral:

$$\int_0^\infty x^{2n}\exp(-\alpha x^2)\,\mathrm{d}x = \frac{(2n-1)!!}{2^{n+1}}\left(\frac{\pi}{\alpha^{2n+1}}\right)^{1/2} \tag{A3.1}$$

Fourier cosine integral:

$$\int_0^\infty x^{\alpha-1}\cos bx\,\mathrm{d}x = \frac{\Gamma(\alpha)}{b^\alpha}\cos\frac{\alpha\pi}{2} \qquad (0<\alpha<1,\quad b>0) \tag{A3.2}$$

When $\alpha = 1/2$, $\Gamma(1/2) = \pi^{1/2}$. Thus,

$$\int_0^\infty x^{-1/2}\cos bx\,\mathrm{d}x = \left(\frac{\pi}{2b}\right)^{1/2} \tag{A3.3}$$

Fourier sine integral:

$$\int_0^\infty x^{\alpha-1}\sin bx\,\mathrm{d}x = \frac{\Gamma(\alpha)}{b^\alpha}\sin\frac{\alpha\pi}{2} \qquad (0<\alpha<1,\quad b>0) \tag{A3.4}$$

For $\alpha = 1/2$,

$$\int_0^\infty x^{-1/2}\sin bx\,\mathrm{d}x = \left(\frac{\pi}{2b}\right)^{1/2} \tag{A3.5}$$

Gamma function:

$$\int_0^\infty x^{\alpha-1}\exp(-x)\,\mathrm{d}x = \Gamma(\alpha) \qquad (\alpha>0) \tag{A3.6}$$

For integral values of α, $\Gamma(\alpha) = (\alpha-1)!$.

Miscellaneous integral:

$$\int_0^\infty \frac{\mathrm{d}x}{x^4 + b^4} = \frac{2^{1/2}\pi}{4b^3} \qquad \text{(A3.7)}$$

A4 SERIES

$$\sum_{n=1}^{\infty} \frac{a}{n^2 + a^2} = -\frac{1}{2a} + \frac{\pi}{2}\coth a\pi \qquad \text{(A4.1)}$$

$$\sum_{n=1}^{\infty} \frac{a}{n^{1/2}(n^2 + a^2)} \cong \int_0^\infty \frac{a}{x^{1/2}(x^2 + a^2)}\,\mathrm{d}x - \int_0^{1/2} \frac{a}{x^{1/2}(x^2 + a^2)}\,\mathrm{d}x$$

$$\cong 2a\int_0^\infty \frac{\mathrm{d}y}{y^4 + a^2} - \frac{1}{a}\int_0^{1/2} \frac{\mathrm{d}x}{x^{1/2}} = \frac{\pi}{(2a)^{1/2}} - \frac{2^{1/2}}{a} \cong \frac{\pi}{(2a)^{1/2}} \qquad (a \gg 1) \qquad \text{(A4.2)}$$