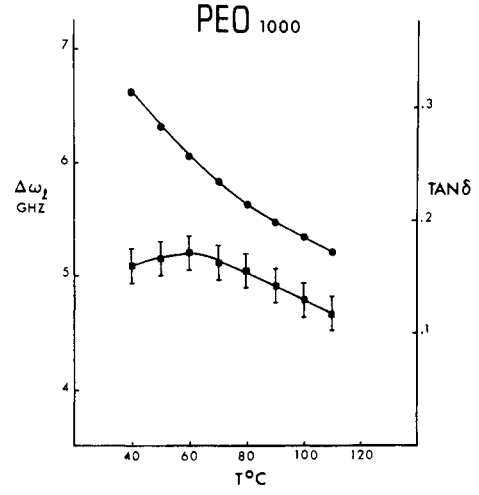

Figure 1. Brillouin frequency $\Delta\omega_l$ (●) and tan δ (■) vs. T for 1000 mol wt poly(ethylene oxide).

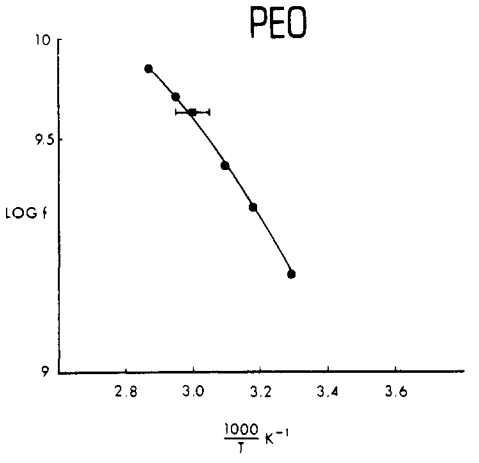

Figure 2. Comparison of dielectric relaxation (●) and hypersonic relaxation (■) in PEO. Log f is plotted vs. $1/T_{max}$.

erable debate.[2,3] One way to gain insight into the amorphous loss processes observed in the semicrystalline state is to measure the loss at high frequencies in the molten state. This approach has been used successfully by Boyd[1,4,5] and coworkers for several highly crystallizable polymers. They found that the temperatures of maximum dielectric loss in the gigahertz frequency range were indeed above the melting point for poly(ethylene oxide). The present study was undertaken to test this result using dynamic mechanical spectroscopy in the hypersonic region. Brillouin scattering was used to obtain the loss data. A value of the frequency and tan δ were determined for longitudinal acoustic phonons as a function of temperature.

Experimental Section

Poly(ethylene oxide) of nominal molecular weight 1000 was obtained from Polysciences, Inc. This polymer was chosen to lower the melting point to $T_m \approx 40$ °C while maintaining the hypersonic loss maximum at its asymptotic value.

Brillouin spectra were obtained as described previously.[6,7] The incident wavelength was 5145 Å and the scattered light was observed at 90°.

Results

The values of $\Delta\omega_l$ (in GHz) and tan δ are plotted vs. temperature in Figure 1. The maximum loss is observed at 60 °C and a frequency of 6.06 GHz. Depression of the melting point allowed measurements down to 40 °C.

The present results are compared to those reported by Porter and Boyd[1] using dielectric relaxation in Figure 2. The log of the frequencies is plotted vs. the reciprocal of the temperatures of maximum loss. The agreement is very good, even on the expanded scale shown here. The loss process is confirmed to be the glass–rubber relaxation.

Observation of a temperature of maximum loss in the hypersonic range above the melting point has previously been reported for bisphenol-A polycarbonate.[7] A dielectric loss maximum has also been observed in molten Nylon 6–10.[4] Examinations of many other crystallizable polymers in the molten state are in progress.

It has been suggested[8] that the frequency of maximum loss at the melting point should be near 10^{12} Hz for the glass–rubber relaxation. For linear polyethylene it appears that this is the case. However, there is no fundamental reason why the melting point should be correlated with the glass–rubber relaxation and the examples cited above serve to illustrate the range of frequencies of maximum loss that are observed near T_m. The present results also suggest that the use of GHz relaxation techniques will be very important in the study of the amorphous loss processes in highly crystallizable polymers.

References and Notes

(1) C. H. Porter and R. H. Boyd, *Macromolecules*, **4**, 589 (1971).
(2) D. W. McCall, *Natl. Bur Stand (U.S.), Spec. Publ.*, **No. 301**, 475–537 (1969).
(3) N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids", Wiley, New York, N.Y., 1967.
(4) R. H. Boyd and C. H. Porter, *J. Polym. Sci., Part A-2*, **10**, 647 (1972).
(5) C. H. Porter, J. H. L. Lawler, and R. H. Boyd, *Macromolecules*, **3**, 308 (1970).
(6) G. D. Patterson, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 455 (1977).
(7) G. D. Patterson, *J. Macromol. Sci., Phys.*, in press.
(8) H. W. Starkweather, *J. Macromol. Sci., Phys.*, **2**, 781 (1968).

Asymptotic Behavior of the Number of Self-Avoiding Walks Terminally Attached to a Surface to which They Never Return

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The effect of excluded volume on the properties of a polymer interacting with a plane surface was first considered by Silberberg,[1] using a theory which was essentially "mean field" in character. One of the parameters needed in this treatment was the exponent which characterized the number of self-avoiding walks which originate at the interface but never return there. This exponent has been estimated by various groups of workers[2–4] using exact enumeration techniques for a variety of lattices. If we consider any three-dimensional lattice in which the surface is represented by a lattice plane, we can write the number of n-step self-avoiding walks which start at an origin in this plane and are then confined to the half space on one side of this plane, as $(n,1)_S$. (The 1 indicates that there is only one vertex in the surface plane.) It has been shown elsewhere[5] that

$$\lim_{n\to\infty} n^{-1} \log (n,1)_S$$

exists and is equal to the connective constant of the lattice, $\log \mu$. In addition there are good reasons to believe that[4]

$$(n,1)_S \sim n^{-\xi}\mu^n$$

Lax and others[2,3] have investigated the value of ξ for the four

Table I
Neville Table for the fccub Lattice

n	$(n,1)_S$	ξ_n	$\xi_n^{(1)}$	$\xi_n^{(2)}$
4	672	0.209 342	0.252 835	
5	6 348	0.222 852	0.277 066	0.294 130
6	60 588	0.233 955	0.283 181	0.298 354
7	582 268	0.242 150	0.290 395	0.292 616
8	5 625 476	0.248 455	0.291 955	0.300 729
9	54 578 380			
10	531 305 396			

Table II
Neville Table for the bccub Lattice

n	$(n,1)_S$	ξ_n	$\xi_n^{(1)}$	$\xi_n^{(2)}$
6	16 104	0.225 569	0.274 073	0.299 326
7	100 504	0.228 968	0.288 701	0.313 456
8	634 960	0.241 204	0.288 109	0.302 145
9	4 004 608	0.243 443	0.294 106	0.300 862
10	25 438 704			
11	161 497 504			

choice cubic and tetrahedral lattices with the conclusion that $\xi \simeq 0.31$, while Middlemiss and Whittington,[4] from enumerations on the cubic, face centered cubic, and tetrahedral lattices, suggested that $0.285 \leq \xi \leq 0.300$. In this paper we present some exact enumeration data on the body centered cubic lattice with the surface plane chosen to be a (distorted) square lattice and we extend the series on the face centered cubic lattice by one additional term. In addition we present Monte Carlo data for walks on the face centered cubic lattice with up to 100 steps.

In attempting to estimate ξ from exact enumeration data it is convenient to make use of ratio methods.[6] Since the values of μ are quite well known (they are estimated to be 6.5295 and 10.035 for the lattices in question[7]) one can estimate ξ from the sequence

$$\xi_n = \tfrac{1}{2}n\{1 - (n + 2,1)_S/\mu^2(n,1)_S\}$$

It is convenient to form extrapolants of the ξ_n by means of a Neville table[6] with entries

$$\xi_n^{(r)} = \{n\xi_n^{(r-1)} - (n - 2r)\xi_{n-2}^{(r-1)}\}/2r$$

with $\xi_n^{(0)} = \xi_n$. The entries for r equal 1 and 2 are given in Tables I and II. The linear extrapolants are well behaved and suggest a value of ξ greater than 0.29 for both lattices. The quadratic extrapolants behave especially well for the body centered cubic case and imply a value of ξ very close to 0.30.

An alternative approach to the estimation of ξ is to use Monte Carlo methods to estimate $(n,1)_S$ for larger values of n. We have used an inversely restricted sampling scheme suggested by Hammersley and Morton[8] and by Rosenbluth and Rosenbluth[9] to estimate $(n,1)_S$ for the face centered cubic lattice for $n \leq 100$; the sample size used was 10 000 walks. Using the previous estimate of 10.035 for the value of μ, ξ can be estimated from the gradient of a log–log plot of $(n,1)_S/\mu^n$ against n. Depending on the number of points used in the least-squares fit this yields values between 0.296 and 0.307. Alternatively, it is clear that $\log\{(n,1)_S/\mu^n\}/\log n$ should tend to $-\xi$ as n becomes large. Indeed it should approach ξ rapidly provided that the amplitude of the singularity is not too far from unity. In this case the values of this quantity range from 0.293 to 0.307 for n between 20 and 100. There is no obvious trend in the data and an unweighted average of the final 30 estimates yields $\xi = 0.302 \pm 0.004$.

These data taken together indicate that the value of ξ is very close to 0.3 and we suggest

$$\xi = 0.300 \pm 0.005$$

as our final, somewhat subjective, estimate.

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References and Notes

(1) A. Silberberg, *J. Chem. Phys.*, **46**, 1105 (1967).
(2) M. Lax, *Macromolecules*, **7**, 660 (1974).
(3) P. Mark, S. Windwer, and M.Lax, *Macromolecules*, **8**, 946 (1975).
(4) K. M. Middlemiss and S. G. Whittington, *J. Chem. Phys.*, **64**, 4684 (1976).
(5) S. G. Whittington, *J. Chem. Phys.*, **63**, 779 (1975).
(6) D. S. Gaunt and A. J. Guttmann, "Phase Transitions and Critical Phenomena", Vol. 3, C. Domb and M. S. Green, Ed., Academic Press, New York, N.Y., 1974.
(7) J. L. Martin, M. F. Sykes, and F. T. Hioe, *J. Chem. Phys.*, **46**, 3478 (1967).
(8) J. M. Hammersley and K. W. Morton, *J. R. Stat. Soc. B*, **16**, 23 (1954).
(9) M. N. Rosenbluth and A. W. Rosenbluth, *J. Chem. Phys.*, **23**, 356 (1955).