CHAPTER 25

Chain Dimensions and Entanglement Spacings

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This chapter summarizes data on chain dimensions and entanglement spacings for a number of linear flexible polymers. The polymers are listed in the Appendix along with their abbreviations used in the Tables. The equations relating various important parameters are from the literature [1–3]. While polymer chain entanglement is far from being understood [4–6], one natural idea based on overlap [7] appears useful for thinking about entanglement effects in polymer melts. This concept leads to the entanglement criterion: *a fixed number of entanglement strands (P_e) share a volume equal to the cube of the tube diameter (a^3)* [8–12]. One of the main purposes of this chapter is to test this criterion using literature data on flexible polymer melts and evaluate this universal number. Empirical relations useful for estimating the plateau modulus and entanglement molar mass of polymer melts emerge from this analysis. Chain entanglement is important, not merely for melt rheology, but also for mechanical properties of glassy [13] and semicrystalline polymers [14]. This chapter first discusses chain dimensions of polymers and then discusses chain entanglement and the tube diameter. The critical molar mass for entanglement effects in melt viscosity is then discussed, followed by the temperature dependence of chain dimensions.

25.1 CHAIN DIMENSIONS

In either the melt state or in a θ-solvent solution, linear flexible polymers adopt Gaussian statistics, and their average conformation is described as a random walk. Consequently, the ratio of their unperturbed mean-square end-to-end distance $<R^2>_0$ and their molar mass M is a constant, for large M, that characterizes their chain dimensions. In practice, the ratio $<R^2>_0/M$ depends weakly on temperature in the melt and the specific choice of θ-solvent, imparting a weak temperature dependence to various quantities calculated from that ratio.

The Kuhn length b of a polymer is the ratio of the mean-square end-to-end distance $<R^2>_0$ and the fully extended size R_{max}

$$b \equiv \frac{\langle R^2 \rangle_0}{R_{max}}. \qquad (25.1)$$

Aliphatic backbone polymers have n backbone bonds, with a well-defined average backbone bond length l, and known backbone bond angle θ, making $R_{max} = nl\cos(\theta/2)$ in the all-*trans* conformation. Flory defined [15] the characteristic ratio C_∞ as the ratio of the actual unperturbed mean-square end-to-end distance $<R^2>_0$ and that of a freely jointed chain nl^2, which is a polymer-specific constant at large M

$$C_\infty \equiv \frac{\langle R^2 \rangle_0}{nl^2} = \frac{m_b \langle R^2 \rangle_0}{l^2 M}. \qquad (25.2)$$

The second equality uses the equation $n = M/m_b$, where m_b is the average molar mass per backbone bond. Using this definition of C_∞, the Kuhn length can be rewritten as:

$$b = \frac{C_\infty nl^2}{nl\cos(\theta/2)} = \frac{C_\infty l}{\cos(\theta/2)}. \qquad (25.3)$$

It is common to assume the fully extended conformation is a linear chain (ignoring bond angles) and hence $R'_{max} = nl$, and $b' = C_\infty l$. Since the bond angle of a polyethylene chain

is $\theta = 68°$, $b'/b = \cos(\theta/2) = 0.83$. In principle, either convention may be utilized; here we use Eq. (25.3) to calculate the Kuhn length.

The Kuhn length is the effective monomer size for the equivalent freely jointed chain (N Kuhn monomers of length b instead of n backbone bonds of length l)

$$\langle R^2 \rangle_0 = C_\infty n l^2 = N b^2, \quad R_{max} = Nb. \quad (25.4)$$

The molar mass of a Kuhn monomer is $M_0 = M/N$ and the volume occupied by the Kuhn monomer is $\nu_0 = M_0/\rho N_{Av}$, where ρ is the density and N_{Av} is Avogadro's number. This description of chain dimensions can be used to calculate many quantities. For example, combining Eqs. (25.3) and (25.4) yields the number of main chain bonds in a Kuhn monomer $n/N = C_\infty / \cos^2(\theta/2)$.

Witten *et al*. [16] define the packing length p as the ratio of the occupied volume of a chain $M/\rho N_{Av}$ and the mean-square end-to-end distance

$$p \equiv \frac{M}{\langle R^2 \rangle_0 \, \rho N_{Av}} = \frac{M_0}{b^2 \rho N_{Av}} = \frac{\nu_0}{b^2}. \quad (25.5)$$

25.2 CHAIN ENTANGLEMENT AND TUBE DIAMETER

The plateau modulus G_e defines the entanglement spacing of a polymer melt, and the entanglement molar mass M_e[17]

$$M_e \equiv \frac{\rho RT}{G_e} = V_e \rho N_{Av}, \quad (25.6)$$

where $R = kN_{Av}$ is the ideal gas constant (k is the Boltzmann constant), T is the absolute temperature, and $V_e \equiv kT/G_e = M_e/(\rho N_{Av})$ is the entanglement volume. The length scale associated with the entanglement spacing is the tube diameter a [3]. Since a chain in the melt is Gaussian on all scales larger than the Kuhn length, and for flexible chains $a \gg b$, the tube diameter is related to the entanglement molar mass through the chain dimensions

$$a = \sqrt{\frac{\langle R^2 \rangle_0 \, M_e}{M}} = b\sqrt{N_e}, \quad (25.7)$$

where N_e is the number of Kuhn monomers in an entanglement strand (of molar mass M_e). The occupied volume of an entanglement strand is V_e

$$V_e = \nu_0 N_e = \nu_0 \left(\frac{a}{b}\right)^2 = a^2 p. \quad (25.8)$$

In analogy to polymer networks (where the equilibrium modulus is kT per network strand) the plateau modulus is kT per entanglement strand

$$G_e = \frac{kT}{V_e} = \frac{b^2 kT}{\nu_0 a^2} = \frac{kT}{a^2 p}. \quad (25.9)$$

The number of entanglement strands P_e within the confinement volume a^3 is determined as the ratio of confinement volume and entanglement strand volume (an overlap parameter [3] for entanglement)

$$P_e \equiv \frac{a^3}{V_e} = \frac{a}{p}. \quad (25.10)$$

This number appears to be constant for flexible polymers, with the average value $P_e = 20.6(\pm 8\%)$. Table 25.1 shows data for polyolefin melts listing density ρ, plateau modulus G_e, melt chain dimensions from SANS $\langle R^2 \rangle_0/M$, entanglement molar mass M_e calculated from Eq. (25.6), Kuhn length b, packing length p, tube diameter a, and the overlap parameter for entanglement P_e, all at temperature T.

Since P_e is apparently a polymer-independent constant, Eq. (25.10) suggests that the tube diameter and packing length are proportional, and the constant of proportionality thus has the empirical temperature dependence [1,2]:

$$a = 14.0 \exp(T/1270) \, p. \quad (25.11)$$

Using Eqs. (25.6), and (25.9)–(25.11), we can obtain useful empirical equations [2] for the entanglement molar mass and the plateau modulus

$$M_e = P_e^2 p^3 \rho N_{Av} = 200 \exp(T/635) \, \rho p^3 N_{Av}, \quad (25.12)$$

$$G_e = \frac{\exp(-T/635)}{200} \frac{kT}{p^3}. \quad (25.13)$$

Table 25.1 lists these quantities for polyolefins. Table 25.2 lists these quantities for polydienes while polyacrylics and polymethacrylics are listed in Table 25.3. Table 25.4 lists these quantities for various other flexible linear polymers.

25.3 CRITICAL MOLECULAR WEIGHT

The critical molar mass (M_c) parameter [18,19] denotes the transition in the melt viscosity/molar mass relation as the exponents change from ~ 1 to ~ 3.4. Table 25.5 presents the polymers for which the M_c values are known while Table 25.6 lists the polymers for which, seemingly, M_c/M_e is one. The ratio of M_c/M_e was long taken to be ~ 2 [18] and thus to be species independent. However, a recent empirical compilation [19] has shown that the ratio is p dependent and varies from ~ 3.5 (PE; $p = 1.69$) to ~ 1.4 (a-PCHE; $p = 5.59$). Based upon the data of Table 25.5 this ratio is empirically expressed as:

$$\frac{M_c}{M_e} = 3.42 p^{-0.534} = \left[\frac{p^*}{p}\right]^{0.534}. \quad (25.14)$$

M_c hence follows the empirical expression:

$$M_c = M_e \left[\frac{p^*}{p}\right]^{0.534}, \quad (25.15)$$

where $M_c = M_e$ at $p = p^* \approx 10$ Å. With M_c expressed in this fashion, M_e overtakes M_c as p approaches p^* in the 10 Å range. At least four polymers exist with $p \cong 10$ Å (see Table

TABLE 25.1. *Molecular characteristics of olefinic polymers and copolymers.*

Polymer	T (K)	ρ (g cm^{-3})	G_e (MPa)	$<R^2>_o/M$ (Å^2)	C_∞	b (Å)	ν_o (Å^3)	M_o	p (Å)	M_e	a (Å)	N_e	P_e
PE	298	0.851	3.5	1.40	8.26	15.4	329	168.3	1.39	602	29.0	3.58	20.8
PE	413	0.785	2.6	1.25	7.38	13.7	318	150.4	1.69	1,040	36.0	6.89	21.3
PEB-2	389	0.802	2.5	1.25	7.70	14.3	339	163.5	1.66	1,040	36.0	6.34	21.7
PEB-2	413	0.785	2.2	1.22	7.51	14.0	338	159.5	1.73	1,220	38.7	7.68	22.3
PEB-5	413	0.788	1.90	1.15	7.47	13.9	353	167.3	1.83	1,420	40.5	8.51	22.1
PEB-7	413	0.789	1.55	1.05	7.08	13.2	347	164.9	1.90	1,750	42.8	10.6	23.0
PEB-10	413	0.791	1.35	1.05	7.53	14.0	391	186.2	2.00	2,010	46.0	10.8	23.0
PEB-12	298	0.860	1.50	1.04	7.72	14.3	382	197.6	1.86	1,420	38.4	7.18	20.7
PEB-12	413	0.793	1.20	0.952	7.06	13.1	379	180.9	2.20	2,270	46.5	12.5	21.1
alt-PEP	298	0.856	1.10	0.924	7.21	13.4	376	194.0	2.10	1,930	42.2	9.93	20.1
alt-PEP	373	0.812	1.03	0.871	6.80	12.6	374	182.9	2.35	2,440	46.1	13.4	19.6
alt-PEP	413	0.790	0.97	0.834	6.51	12.1	368	175.1	2.52	2,790	48.3	16.0	19.2
PEB-18	298	0.860	1.12	0.926	7.42	13.8	396	205.1	2.09	1,900	42.0	9.27	20.1
PEB-18	413	0.797	0.90	0.913	7.31	13.6	421	202.2	2.28	3,040	52.7	15.0	23.1
HPI-16	373	0.812	0.88	0.813	6.51	12.1	368	180.1	2.52	2,860	48.2	15.9	19.2
HPI-20	373	0.812	0.79	0.788	6.45	12.0	372	181.9	2.60	3,190	50.1	17.5	19.3
PEB-25	298	0.864	0.69	0.800	7.08	13.2	416	216.4	2.40	3,100	49.8	14.3	20.7
PEB-25	413	0.799	0.67	0.799	7.07	13.1	449	216.2	2.60	4,090	57.2	18.9	22.0
a-PP	298	0.852	0.48	0.678	6.00	11.2	358	183.4	2.88	4,390	54.6	23.9	19.0
a-PP	348	0.825	0.48	0.678	6.00	11.2	369	183.4	2.97	4,970	58.1	27.1	19.5
a-PP	413	0.791	0.47	0.678	6.00	11.2	385	183.4	3.10	5,780	62.6	31.5	20.2
a-PP	463	0.765	0.42	0.678	6.00	11.2	398	183.4	3.20	7,010	68.9	38.2	21.5
i-PP	463	0.766	0.43	0.694	6.15	11.4	407	187.8	3.12	6,850	69.0	36.5	22.1
s-PP	463	0.766	1.35	1.03	9.12	16.9	604	278.7	2.10	2,180	47.4	7.83	22.5
HHPP	298	0.878	0.52	0.691	6.12	11.4	353	187.0	2.74	4,180	53.8	22.4	19.6
HHPP	413	0.810	0.52	0.691	6.12	11.4	383	187.0	2.97	5,350	60.8	28.6	20.5
HPI-34	373	0.812	0.50	0.703	6.25	11.6	392	192.0	2.91	5,030	59.5	26.2	20.4
alt-PEB	298	0.861	0.58	0.725	6.88	12.8	434	225.2	2.66	3,680	51.6	16.3	19.4
alt-PEB	413	0.800	0.52	0.692	6.57	12.2	446	214.9	3.00	5,280	60.4	24.6	20.1
PEB-32	298	0.863	0.44	0.641	6.22	11.5	400	208.0	3.00	4,860	55.8	23.3	18.6
PEB-32	413	0.802	0.43	0.692	6.71	12.5	465	224.6	2.99	6,400	66.6	28.5	22.2
HPI-50	373	0.812	0.35	0.632	6.21	11.5	430	210.5	3.24	7,190	67.4	34.2	20.8
PEB-40	298	0.864	0.24	0.570	6.06	11.3	427	222.1	3.37	8,910	71.3	40.1	21.1
PEB-40	413	0.805	0.30	0.595	6.32	11.7	478	231.8	3.47	9,210	74.0	39.7	21.3
PIB	298	0.918	0.34	0.570	6.73	12.5	496	274.2	3.18	6,690	61.7	24.4	19.4
PIB	413	0.849	0.30	0.557	6.58	12.2	524	267.9	3.51	9,710	73.6	36.3	20.9
a-PEE	298	0.866	0.18	0.480	5.67	10.5	443	230.9	4.00	11,900	75.6	51.6	18.9
a-PEE	413	0.807	0.20	0.508	6.00	11.1	503	244.3	4.05	13,800	83.9	56.7	20.7
HPI-75	300	0.855	0.12	0.452	6.67	12.4	660	339.7	4.30	17,800	89.6	52.3	20.8
HPMYRC	324	0.832	0.12	0.434	6.73	12.5	720	360.6	4.60	18,700	90.0	51.8	19.6
a-PHEX	273	0.871	0.14	0.542	9.60	17.8	1119	586.6	3.52	14,100	87.5	24.1	24.9
HPMYRC-64	308	0.871	0.10	0.409	7.36	13.7	895	457.5	4.78	21,700	94.3	47.5	19.7
a-PCHE	433	0.920	0.068	0.323	7.49	13.9	1082	599.4	5.59	48,700	125.4	81.2	22.4

TABLE 25.2. *Molecular characteristics of polydiene polymers and copolymers.*

Polymer	T (K)	ρ (g cm^{-3})	G_e (MPa)	$<R^2>_o/M$ (Å^2)	C_∞	b (Å)	ν_o (Å^3)	M_o	p (Å)	M_e	a (Å)	N_e	P_e
cis-PI	298	0.910	0.58	0.679	5.20	9.34	235	128.6	2.69	3,890	51.4	30.2	19.1
PI-7	298	0.900	0.35	0.596	4.70	8.44	221	119.6	3.10	6,370	61.6	53.2	19.9
PI-16	298	0.899	0.35	0.593	4.88	8.82	243	131.2	3.12	6,360	61.4	48.5	19.8
PI-20	298	0.898	0.35	0.591	4.96	8.98	253	136.5	3.13	6,350	61.3	46.5	19.6
PI-29	298	0.896	0.35	0.587	5.20	9.39	279	150.3	3.16	6,340	61.0	42.2	19.3

TABLE 25.2. *Continued.*

Polymer	T (K)	ρ (g cm^{-3})	G_e (MPa)	$<R^2>_o/M$ (Å^2)	C_∞	b (Å)	ν_o (Å^3)	M_o	p (Å)	M_e	a (Å)	N_e	P_e
PI-34	298	0.895	0.35	0.585	5.26	9.58	291	156.9	3.17	6,330	60.9	40.4	19.2
PI-50	298	0.893	0.41	0.528	4.80	8.80	273	146.6	3.52	5,390	53.4	36.8	15.1*
PI-75	298	0.890	0.37	0.563	8.07	15.0	745	399.3	3.32	5,960	57.9	14.9	17.5
cis-PBd	298	0.900	0.76	0.758	4.61	8.28	167	90.5	2.44	2,930	47.1	32.4	19.4
PBd-7	298	0.895	1.15	0.876	5.52	9.93	209	112.5	2.12	1,930	41.1	17.1	19.4
PBd-15	298	0.896	1.10	0.854	5.54	10.0	218	117.7	2.17	2,020	41.5	17.1	19.1
PBd-18	298	0.895	1.05	0.846	5.56	10.1	222	119.8	2.19	2,110	42.3	17.6	19.3
PBd-20	298	0.895	1.07	0.841	5.61	10.1	227	122.4	2.21	2,070	41.7	16.9	18.9
PBd-23	298	0.895	1.05	0.832	5.66	10.2	234	125.9	2.23	2,110	41.9	16.8	18.8
PBd-26	298	0.895	1.00	0.824	5.68	10.3	238	128.0	2.25	2,220	42.7	17.3	19.0
PBd-30	298	0.894	0.98	0.813	5.67	10.3	244	131.2	2.28	2,260	42.9	17.2	18.8
PBd-62	298	0.890	0.81	0.727	6.17	11.3	328	175.9	2.57	2,720	44.5	15.5	17.4
PBd-98	300	0.890	0.57	0.661	7.39	13.7	532	284.8	2.82	3,890	50.7	13.7	18.0
SBR**	298	0.913	0.78	0.818	6.41	11.9	316	173.6	2.22	2,900	48.7	16.7	22.0
PEBd	298	0.891	0.29	0.543	4.85	9.02	279	149.7	3.43	7,610	64.3	50.8	18.7
55-DMBD	348	0.861	0.33	0.640	7.31	13.6	556	288.4	3.01	7,550	69.5	26.2	23.1
PMYRC-0	298	0.892	0.10	0.398	5.30	9.85	454	243.8	4.68	22,100	93.8	90.6	20.0
PMYRC-64	298	0.891	0.071	0.374	5.87	10.9	592	317.5	4.98	31,100	107.8	97.9	21.7

*The low value of P_e likely indicates the real plateau modulus is lower.
**Styrene content 25 wt%.

TABLE 25.3. *Molecular characteristics of poly(acrylics) and poly(methacrylics).*

Polymer	T (K)	ρ (g cm^{-3})	G_e (MPa)	$<R^2>_o/M$ (Å^2)	C_∞	b (Å)	ν_o (Å^3)	M_o	p (Å)	M_e	a (Å)	N_e	P_e
a-PMA	298	1.11	0.25	0.436	7.91	14.7	740	494.6	3.43	11,000	69.2	22.2	20.2
a-PEA	298	1.13	0.36	0.463	9.76	18.1	1,040	710.1	3.17	7,770	60.0	10.9	18.9
a-POA	298	0.98	0.16	0.442	17.1	31.9	3,890	2,295	3.83	15,200	81.9	6.61	21.4
a-PMMA	413	1.13	0.31	0.390	8.22	15.3	880	598	3.77	12,500	69.9	20.9	18.5
a-PEBMA	373	0.988	0.15	0.315	11.3	21.0	2,350	1,396	5.34	20,400	80.2	14.6	15.0*
a-PHMA	373	0.960	0.090	0.366	13.1	24.4	2,800	1,622	4.73	33,100	110.0	20.4	23.3
a-POMA	373	0.923	0.033	0.272	11.4	21.1	2,950	1,635	6.61	86,700	153.6	53.0	23.2
a-PDDMA	298	0.929	0.016	0.254	13.6	25.3	4,500	2,513	7.04	144,000	191.1	57.2	27.1*
a-PAPHMA	393	1.00	0.012	0.167	14.5	26.9	7,220	4,348	9.95	272,000	213.2	62.6	21.4
a-PBPHMA	393	1.00	0.0092	0.154	15.2	28.2	8,600	5,173	10.8	355,000	233.8	68.6	21.7

*These two samples yield P_e values at odds with the value of $\sim$21. This indicates the potential presence of pronounced errors in the chain dimension and/or plateau modulus values. From the trend shown in the chain dimension column the primary error seems to exist with this parameter.

TABLE 25.4. *Molecular characteristics of miscellaneous polymers.*

Polymer	T (K)	ρ(g cm^{-3})	G_e(MPa)	$<R^2>_o/M$ (Å^2)	p (Å)	M_e	a (Å)	P_e
a-PαMS	473	1.04	0.32	0.442	3.61	12,800	75.1	20.8
a-PS	413	0.969	0.20	0.437	3.92	16,600	85.2	21.7
i-PS	413	0.969	0.19	0.420	4.08	17,500	85.7	21.0
a-PtBS	473	0.957	0.10	0.361	4.81	37,600	116.5	24.2
a-PVA	333	1.08	0.35	0.490	3.14	8,540	64.7	20.6
a-PVME	303	1.05	0.41	0.580	2.73	6,450	61.2	22.4
m-AEK	473	1.20	2.2	0.775	1.79	2,140	40.8	22.8
Me-PEEK	463	1.16	3.3	0.834	1.72	1,350	33.6	19.6
PC	473	1.14	2.7	0.864	1.69	1,660	37.9	22.5

TABLE 25.4. *Continued.*

Polymer	T (K)	ρ (g cm^{-3})	G_e (MPa)	$<R^2>_o/M$ (Å^2)	p (Å)	M_e	a (Å)	P_e
PDMS	298	0.970	0.20	0.422	4.06	12,000	71.2	17.5
PET	548	0.989	3.1	0.845	1.99	1,450	35.0	17.6
PN6	543	0.985	1.8	0.853	1.98	2,470	45.9	23.2
PEO	353	1.06	1.8	0.805	1.95	1,730	37.3	19.2
POM	473	1.14	1.7	0.763	1.91	2,640	44.8	23.5
PPO	505	0.998	1.2	0.741	2.24	3,500	50.9	22.7
PSF	523	1.15	2.1	0.756	1.91	2,380	42.4	22.2
PTFE	653	1.46	1.7	0.598	1.90	4,660	52.8	27.7
RADEL-R	555	1.22	3.6	0.821	1.66	1,560	35.8	21.6

TABLE 25.5. *Entanglement and critical molecular weights of miscellaneous polymers.*

Polymer	T (K)	ρ (g cm^{-3})	$<R^2>_o/M$ (Å^2)	p (Å)	M_e	M_c	M_c/M_e
PE	443	0.768	1.21	1.79	980**	3,480	3.5
PBd-7	298	0.895	0.876	2.12	2,000	6,380	3.2
PI-7	243	0.919	0.618	2.92	3,250*	10,000	3.0
PEO	353	1.081	0.805	1.91	2,000	5,870	2.9
SBR	298	0.930	0.708	2.52	2,960	8,210	2.8
a-PVA	428	1.08	0.490	3.14	9,100	24,500	2.7
alt-PEP	373	0.812	0.871	2.40	3,100	8,100	2.6
PI-7	298	0.900	0.625	2.95	6,025	13,100	2.2
a-PMMA	490	1.09	0.425	3.58	13,600	29,500	2.2
PBd-98	300	0.889	0.720	2.59	3,850	8,200	2.1
a-PαMS	459	1.04	0.460	3.47	13,300	28,000	2.1
PDMS	298	0.970	0.422	4.06	12,000	24,500	2.0
PIB	298	0.918	0.570	3.17	6,900	13,100	1.9
a-PS	490	0.959	0.434	3.39	18,100	31,200	1.7
PIB	490	0.817	0.570	3.57	10,500	17,000	1.6
a-PCHE	453	0.920	0.323	5.59	48,750	80,000	1.6

*Calculated value is 6,000.
**Measured value at 413 K. The calculated value (via Eq. (25.12)) at 443 K is 1,150.

TABLE 25.6. *Polymers with large packing lengths.*

Polymer	T (K)	ρ (g cm^{-3})	$<R^2>_o/M$ (Å^2)	p (Å)	M_e	$[M_c/M_e]$
a-PHDEC	418	0.796	0.213	9.79	173,000*	1.01**
a-PAPHMA	393	1.0	0.167	9.94	268,000	1.00
a-PBPHMA	393	1.0	0.154	10.8	355,000	0.96
PMA-CH3	363	1.17	0.123	11.5	485,000*	0.93

*Via Eq. (25.12).
**Via Eq. (25.15).

25.6). Since it seems improbable that $M_e > M_c$ for any polymer, we expect the limiting value for M_c/M_e of 1, independent of p for $p \geq 10$ Å. An unexplained facet of these empirical observations is that as p increases, fewer entanglement events are seemingly required to reach the regime where the melt viscosity becomes proportional to the 3.4 power of molar mass. This is displayed in Table 25.5 where the M_e and M_c data for various flexible polymers are listed. Note that while the relation between M_e and packing length is understood [1], the corresponding state of play between p and M_c remains purely empirical [19].

25.4 TEMPERATURE DEPENDENCE OF CHAIN DIMENSIONS

A feature of chain dimensions is their temperature dependence that is expressed in terms of

$$\kappa \equiv \frac{d \ln \langle R^2 \rangle_0}{dT} = \frac{f_e/f}{T} \qquad (25.16)$$

where f_e/f denotes the energetic fraction of the temperature-dependent force in a polymer network at constant volume.

TABLE 25.7. *Melt state values of $\kappa = d \ln <R^2>_0/dT$.*

Polymer samples	$\kappa \times 10^3 (K^{-1})$	
	From SANS	From f_e/f
alt-PEP (PEP)*	−1.1 [25]	−1.5 [26,27]
HPI-50	−0.2 [21]	—-
a-PCHE	∼0 [21]	—
a-PEE	+0.40 [28,29]	+0.30 [30]
a-PMMA	+0.10 [31]	−0.10 [24]
a-PP	−0.1 [32]	—-
a-PS	∼0 [31]	+0.17 [33,34]
a-PPEN	—–	+0.33 [30]
alt-PEB	0 [21]	—-
HHPP	0 [21]	—–
i-PP	∼0 [35]	—-
PBd-7	—–	+0.16 [36]
PDMS	—–	+0.78 [37]
PEB-2(PE)	−1.2 [38]	−1.2 [39]
PEB-5	−1.3 [29]	—-
PEB-7	−0.65 [29]	—–
PEB-10	−0.44 [29]	—–
PEB-12	−0.44 [29]	—–
PEB-18	−0.1 [29]	—–
PEB-25	0 [29]	—–
PEB-32	+0.63 [29]	—–
PEB-40	+0.55 [29]	—–
PEO	−0.30 [40]	+0.03 [41]
PIB	—–	−0.28 [42]
HPI-75	+1.2 [21]	—-
PI-7 (*cis*-PI)	+0.40 [21]	+0.41 [43]

*Ethylene–propylene random copolymer.

The empirical sign of κ can be +, 0, or – (see Table 25.7). The modes of measurement have included theta condition measurements utilizing a family of theta solvents or melt state measurements. The latter include thermoelastic measurements on networks [22] and small angle neutron scattering (SANS) measurements on labeled chains in a polymer melt [23]. Generally, the theta condition approach (multiple theta solvents over a wide temperature range) is recognized to be unreliable [21,24]. An example of this [21] is *a*-PEE, where extensive theta condition work (over the temperature range of ∼200 K) led to a negative value of $\kappa = -1.2 \times 10^{-3}$ K^{-1}, as opposed to the two positive values found for the melt state by SANS and thermoelastic measurements; see Table 25.7. The role of κ on the packing length, plateau modulus and entanglement volume can be significant, particularly for cases where the melt rheology is studied over a wide temperature range. A 200 K range is common for amorphous polymers having low glass transition temperatures.

The packing length has two sources of temperature dependence ($<R^2>_0$ and ρ, see Eq. (25.5)). For typical temperatures (350 K) the change in density for polymer liquids as a function of temperature is $d \ln \rho/dT \approx -6 \times 10^{-4}$ K^{-1}. $<R^2>_0$ is the more interesting parameter, in that it can increase, decrease, or remain constant as temperature is changed.

APPENDIX *Alphabetical Listing of Polymers.*

Name	References	Description
alt-PEB	[44,45]	essentially alternating poly(ethylene-*co*-1-butene); hydrogenated PEBd
alt-PEP	[25,46,47]	essentially alternating poly(ethylene-*co*-propylene); hydrogenated PI-7
a-PαMS	[1,17,18,48,49]	atactic poly(α-methyl styrene)
a-PAPHMA	[50,51]	atactic poly[6-{4(anisyloxycarbonyl)phenoxy}-hexyl methacrylate]
a-PBPHMA	[50,51]	atactic poly[6-{4(butoxycarbonyl)phenoxy}-hexyl methacrylate]
a-PCHE	[1,19,21,52]	atactic poly(cyclohexyl)ethylene or poly(vinyl cyclohexane)
a-PDDMA	[53,54]	atactic poly(dodecyl)methacrylate
a-PEA	[53,55]	atactic poly(ethyl)acrylate
a-PEBMA	[17,53,56]	atactic poly(ethyl butyl)methacrylate
a-PEE	[28,57]	atactic poly(ethyl ethylene); also called poly(butene-1);may be made via the hydrogenation of poly(vinyl ethylene)
a-PHDEC	[58]	atactic poly(hexadecene-1)
a-PHEX	[59,60]	atactic poly(hexene-1)
a-PHMA	[53,61]	atactic poly(hexyl)methacrylate
a-PMA	[55,62]	atactic poly(methyl)acrylate
a-PMMA	[17,18,21,31,63]	atactic poly(methyl)methacrylate
a-POA	[55,59]	atactic poly(octyl)acrylate
a-POMA	[17,53,54,64]	atactic poly(octylmethyl)methacrylate
a-PP	[32,65,66]	atactic polypropylene; hydrogenated poly(2-methyl 1,3-pentadiene)
a-PPEN	[59]	atactic poly(pentene-1)
a-PS	[17–19,31,67]	atactic polystyrene
a-PtBS	[1,68]	atactic poly(*t*-butyl styrene)

APPENDIX *Continued.*

Name	References	Description
a-PVA	[17,18,54]	atactic poly(vinyl acetate)
a-PVME	[69,70]	atactic poly(vinyl-methylether)
cis-PBd	[17,71]	1,4-polybutadiene ~ 96% *cis* content.
cis-PI	[17,72,73]	1,4-polyisoprene ~ 100% *cis* content; natural rubber
55-DMBD	[1]	poly-2,3(dimethyl butadiene) 55% 1,4; 45% 3,4 content.
HHPP	[1,21,45]	hydrogenated poly(2,3 dimethyl)butadiene:head-to-head polypropylene (alternating copolymer of ethylene and butene-2).
HPI-*x*	[1,26,74]	hydrogenated polyisoprene where *x* = 3,4 content of parent polyisoprene
HPMYRC-*x*	[1,45]	hydrogenated poly(myrcene) with *x*% 3,4
i-PMMA	[54,63]	isotactic-poly(methylmethacrylate)
i-PP	[35,66]	isotactic polypropylene
i-PS	[54,75]	isotactic polystyrene
m-AEK	[76]	poly(*m*-arylene–ether–ketone)
Me-PEEK	[77,78]	methyl-poly(aryl–ether–ether–ketone); prepared from methyl hydroquinone and 4,4′-difluorobenzophenone.
PBd-*x*	[57,79–82]	polybutadiene, *x* = vinyl percent; for 100% vinyl content the material is identified as poly(vinyl ethylene) or 1,2-polybutadiene.
PC	[1,54,76,83,84]	polycarbonate of bisphenol A(4, 4'-isopropylidenediphenol)
PDMS	[17,85–87]	poly(dimethylsiloxane)
PE	[17,19,38,88–90]	polyethylene
PEBd	[1,44]	poly(ethyl butadiene) ~ 75/20/5 *cis*/*trans*/3,4
PEB-*x*	[29,57]	poly(ethylene–butene) random copolymer; *x* denotes number of ethyl branches per 100 backbone carbons
PEO	[18,19,40]	poly(ethylene oxide)
PET	[54,91,92]	poly(ethylene terephthalate)
PIB	[17,18,93–95]	polyisobutylene
PI-*x*	[21,47,96–98]	1,4-polyisoprene where *x* = 3,4 content; PI-75 is 75% 3,4, and 25% 1,2 (with essentially no 1,4 addition)
PMA-CH3	[99]	main-chain liquid crystal polyester
PMYRC-*x*	[1,44,45]	poly(myrcene) with *x*% 3,4 [myrcene = 1,6-octadiene-7-methyl-3-methylene]
PN6	[54,100,101]	polycaprolactam-nylon 6
POM	[28,54]	poly(oxymethylene)
PPO	[76,102]	poly(phenylene oxide)
PSF	[76,103]	alternating copolymer of bisphenol A and dichlorodiphenyl sulfone (UDEL)
PTFE	[104,105]	poly(tetrafluoro)ethylene
RADEL-R	[76,103]	alternating copolymer of 4,4′-biphenol and dichlorodiphenyl sulfone
SBR	[17,106]	solution prepared copolymer (anionic polymerization) styrene–butadiene (34% vinyl; 19% *cis* and 47% *trans*) 25 wt% styrene
s-PP	[66,107,108]	syndiotactic polypropylene

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