Hydrodynamic radius and dynamic scattering from randomly crosslinked chains

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The path-weighting generating function (pwgf) method is applied to calculate the hydrodynamic radii of the randomly crosslinked system as well as its monodisperse faction. Exactly the same relation is found for the z-average reciprocal effective hydrodynamic radius of the linear and the randomly crosslinked system as a function of the weight-average degree of polymerization DP_w, where $b\langle R_h^{-1}\rangle_z = C(DP_w)^{-1/2}$ with a constant C depending on the primary chain distribution. The weight-average reciprocal effective hydrodynamic radius, however, depends on the number average degree of polymerization and only moderately changes with crosslinking. The effective hydrodynamic radius of the monodisperse fraction is proportional to the quadratic root of the number of crosslinks. The technique is also applied to the dynamic scattering where formulae for the preaveraged and the non-preaveraged first cumulants are given.

INTRODUCTION

The complexities in a real branched polymer system are due to heterodispersities with respect to molecular weights as well as branched structures. Although the development in the polymerization technique enables one to prepare any polymer of well-defined structure, the randomly branched polymer system still has a practical importance. There have been several attempts made for the calculations of the unperturbed dimensions of random flight branched molecules which are monodisperse with respect to both the number of branch units per molecule and the molecular weight[1-3]. The branch units in these models are distributed either uniformly or randomly, and the functionality of the branch units is fixed. These calculations are straightforward but cumbersome. The difficulties in these calculations are mainly due to the combinatorial nature, which may be reduced by the adaptation of the generating function (gf) method (Good's stochastic theory of cascade processes[4]) as shown by Gordon[5] for Stockmayer's[6] and Flory's theories of gelation. The path-weighting generating function (pwgf), first introduced for the calculation of the particle scattering factors of the randomly branched polycondensates[8], also provides a simple method for combinatorial calculations[9,10] and this method has been expanded to deal with branched polymer systems which are produced by random crosslinking ('vulcanization') of primary chain population[11,12].

This method is now applied to calculate the hydrodynamic properties of randomly crosslinked polymer systems where special attention is paid to the quasielastic light scattering from these systems with regard to the recent development of the laser light scattering technique. The isomeric averages of some statistical quantities of the monodisperse fraction from the randomly crosslinked systems are calculated with the aid of Lagrange's expansion method[15,16] so as to estimate the relative contributions of crosslinking and polydispersity to their physical (especially hydrodynamic) properties.

THEORETICAL BACKGROUND

The system treated here is that of branched polymers produced by random crosslinking. The pwfg for this system is written in terms of bivariate gf as[12]

$$u_0(\{\theta\}) = \sum_{y7_0=1}^{\infty} m_{y_0}\theta_1{}^{y_0}\theta_2{}^{B_0(\varphi;y_0)}(1-\alpha+\alpha u_1(\{\theta\}))^{y_0} \tag{1}$$

with

$$u_i(\{\theta\}) = \sum_{y_i=1}^{\infty} m_{y_i}\theta_1{}^{y_i}\theta_2{}^{B_i(\varphi;y_0y_1,\ldots y_i)}(1-\alpha+\alpha u_{i+1}(\{\theta\}))^{y_i-1} \tag{2}$$

where m_y denotes the weight fraction of y-mers in the primary distribution and α is the fraction of crosslinks per primary chain. The auxiliary variable θ_1 stores the genetic information of crosslinks in the system and $B_i(\varphi;y_0,y_1,\ldots,y_i)$ is the enumeration gf where the coefficient of φ specifies the mean number of paths (linear progressions) of the length n (where n is the number of bonds between monomeric repeat units, see *Figure 1*), and each such path connects a unit on the zeroth generation, called the root, and a unit on generation i ($i=0$, 1, 2,...)[11,12]:

$$B_i(\varphi;y_0,y_1,\ldots,y_i) = \varphi^i[B_0(\varphi;y_0)][B_0(\varphi;y_i)]\prod_{s=1}^{i-1}[B_0(\varphi;y_s)-1]\Big/(y_s-1) \tag{3}$$

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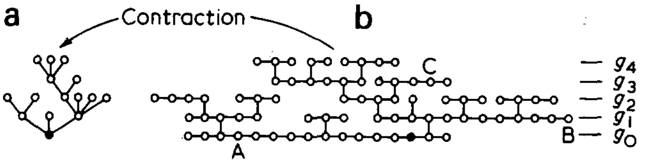

Figure 1 **Crosslinked tree (b) and its contracted form (a), with the root being marked ●. A, B and C specify the paths of length 10 from the root on the 0th, the 1st and the 3rd generations respectively**

where

$$B_0(\varphi;y)=\frac{1}{y}\left[\frac{y(1+\varphi)}{1-\varphi}-\frac{2\varphi(1-\varphi^y)}{(1-\varphi)^2}\right] \qquad (4)$$

and the auxiliary variable φ restores the information on the path length. Differentiation of equation (2) with respect to θ_2 at $\theta_2=1$ yields a new enumeration gf for the mean number of distinct paths from a root chosen at random in the whole ensemble, i.e.,

$$E(\theta_1,\varphi)=\sum m_y\theta_1{}^yB_0(\varphi;y)(1-\alpha+\alpha u)^y$$
$$+\frac{\alpha\varphi[\sum m_y\theta_1{}^yB_0(\varphi;y)(1-\alpha+\alpha u)^{y-1}]^2}{1-\alpha\varphi[\sum m_y\theta_1{}^y\{B_0(\varphi;y_1-1\}(1-\alpha+\alpha u)^{y-2}]} \qquad (5)$$

where

$$u\equiv u_1(\theta_1,1)=u_2(\theta_1,1)=\ldots=\sum m_y\theta_1{}^y(1-\alpha+\alpha u)^{y-1} \quad (6)$$

The utility of this gf was demonstrated in the preceeding paper[12] where the various averages of degrees of polymerization have been calculated as well as the mean-square radius of gyration $\langle S^2\rangle_z$ and the particle scattering factor $P_z(q)$. When φ is made equal to 1 in equation (5) (where $B_0(\varphi;y)=1$), then equation (5) reduces by definition to the weight-fraction gf of the system whose integral or differential with respect to θ_1 at $\theta_1=1$ gives, respectively, the number-average (DP_n) or the weight-average (DP_w) degree of polymerization:

$$DP_n=\bar{y}_n/(1-\alpha\bar{y}_n/2) \qquad (7)$$

or

$$DP_w=\bar{y}_w(1+\alpha)/\{1-\alpha(\bar{y}_w-1)\} \qquad (8)$$

where $\bar{y}_w$ and $\bar{y}_n$ are the number-average and the weight-average degrees of polymerization of the primary chains. For Gaussian chains where the distance between two repeat units is proportional to the number of repeat units between the two, the z-average particle scattering factor is directly calculated from equation (5) by allowing

$$\varphi=\exp(-q^2b^2/6) \qquad (9)$$

as

$$DP_wP_z(q)=(1+\alpha\varphi)\bar{f}_w(\varphi)\Big/[1-(\bar{f}_w(\varphi)-1)\alpha\varphi] \qquad (10)$$

and the z-average radius of gyration is given by $(b^2/2)(\partial P_z(q)/\partial\varphi)_{\phi=1}$ as

$$\langle S^2\rangle_z\simeq\frac{b^2}{6}\frac{\bar{y}_z}{y_w}DP_w \qquad (11)$$

where the variable q gives the magnitude of the scattering vector $\mathbf{q}$ as

$$q=(4\pi/\lambda)\sin(\Theta/2) \qquad (12)$$

Θ, the scattering angle; λ, the wavelength of the incident beam; with b^2 and $\bar{y}_z$ denoting the mean-square distance between two adjacent repeat units and the z-average degree of polymerization of primary chains respectively. Equation (10) is effected by introducing the function $\bar{f}_w(\varphi)$. This is defined as

$$\bar{f}_w(\varphi)=\sum m_yB_0(\varphi;y) \qquad (13)$$

and the concrete calculations for specified primary chain distributions are based on this new function $\bar{f}_w(\varphi)$. Expressed in terms of the number fraction gf of the primary distribution $N(\varphi)$ ($\equiv\Sigma n_y\varphi^y$), this is defined as

$$\bar{f}_w(\varphi)=\frac{1+\varphi}{1-\varphi}-\frac{2\varphi}{(1-\varphi)^2\bar{y}_n}[1-N(\varphi)] \qquad (14)$$

with φ given by equation (9) in this particular example. The number fraction n and the weight fraction m (e.g., in equations (1) and (2)) are generally related as

$$m_y=n_yy/\sum n_yy=n_yy/\bar{y}_n=n_yy/N'(1) \qquad (15)$$

Alternatively, in terms of the gf's, the weight fraction gf $W(\varphi)$ ($\equiv\Sigma m_y\varphi^y$) is given by the number fraction gf $N(\varphi)$ as

$$W(\varphi)=\varphi N'(\varphi)/N'(1) \qquad (16)$$

Table 1 in ref. 11 summarizes the function $\bar{f}_w(\varphi)$ for various primary chain distributions to facilitate further calculations. The function $\bar{f}_w(\varphi)$ corresponds to the enumeration gf for the mean number of distinct paths with the auxiliary variable φ in the primary chain itself, which is indicated by placing $\alpha=0$ in equation (5).

EFFECTIVE HYDRODYNAMIC RADIUS

This section deals with the effective hydrodynamic radii or the translational diffusion coefficients of the randomly crosslinked system in terms of two types of ensemble averages (i.e., the z-average and the weight-average). Application to the angular dependence of the quasielastic scattering (first cumulant) is shown in a later section.

The translational diffusion coefficient D of an x-mer is given according to Kirkwood[13] as

$$D/k_BT=(x\zeta_0)^{-1}+(6\pi\eta_0x^2)^{-1}\sum_{i,j}\langle R_{ij}{}^{-1}\rangle \qquad (17)$$

where ζ_0 and η_0 are the friction coefficient of a monomer unit and the solvent viscosity respectively, and the sum of the configurational average of the reciprocal of the distance between the i-th and the j-th unit extends over all pairs of units in a molecule. In the limiting case of non-draining, the first term on the right side of equation (17) may be negligible and the hydrodynamic radius (Stokes radius) R_h is defined as

$$R_h{}^{-1}\equiv(6n\eta_0/k_BT)D=x^{-2}\sum_{(i,j)}\langle R_{ij}{}^{-1}\rangle \qquad (18)$$

Depending on the method of experimental determination, the observable quantities D or R_h^{-1} are subject to various types of ensemble averages. For example, the quasielastic light scattering measurement yields the z-average translational diffusion coefficient (or the z-average of the reciprocal effective hydrodynamic radius), while the corresponding weight-average is measured in the conventional transport process of boundary spreading (diffusion experiment).

The z-average and the weight-average reciprocal effective hydrodynamic radii are given by definition as

$$\langle R_h^{-1}\rangle_z DP_w \equiv \sum_x w_x x^{-1} \sum_{(i,j)} \langle R_{ij}^{-1}\rangle \tag{19}$$

$$\langle R_h^{-1}\rangle_w \equiv \sum_x w_x x^{-2} \sum_{(i,j)} \langle R_{ij}^{-1}\rangle \tag{20}$$

which are transmitted, with the Gaussian subchain approximation

$$\langle R_{ij}^{-1}\rangle = b^{-1}(6/\pi)^{1/2}(|i-j|)^{-1/2} \tag{21}$$

and the relationship

$$n^{-1/2} = 2\pi^{-1/2}\int_0^\infty \exp(-n\beta^2)\mathrm{d}\beta \tag{22}$$

respectively, into equations (23) and (24), a form to facilitate evaluation of the sums by the cascade theory. Thus,

$$\langle R_h^{-1}\rangle_z DP_w = (2\sqrt{6}/\pi)b^{-1}\int_0^\infty \sum_x w_x x^{-1} \sum_{\text{all } n\text{'s}} [\exp(-\beta^2)^n \mathrm{d}\beta \tag{23}$$

$$\langle R_h^{-1}\rangle_w = (2\sqrt{6}/\pi)b^{-1}\int_0^\infty \sum_x w_x x^{-2} \sum_{\text{all } n\text{'s}} [\exp(-\beta^2)]^n \mathrm{d}\beta \tag{24}$$

Here the notation 'all n's' denotes summation over all possible distinct paths (linear progression) between pairs of repeat units in the system. The mean number of distinct paths in a whole ensemble is obtained from the enumeration gf in equation (5). Thus the z-average reciprocal effective hydrodynamic radius is given as

$$\langle R_h^{-1}\rangle_z DP_w = 2(\sqrt{6}/\pi)b^{-1}\int_0^\infty \mathrm{d}\beta\{(1+\alpha\varphi)\bar{f}_w(\varphi)/[1-\alpha\varphi(\bar{f}_w(\varphi)-1)]-1\} \tag{25}$$

where $\bar{f}_w(\varphi)$ is defined by equation (13) and

$$\varphi \equiv \exp(-\beta^2) \tag{26}$$

The constant term 1 should be subtracted to eliminate the contribution of R_{ii}^{-1} (the distance O). Similarly, the weight-average reciprocal effective hydrodynamic radius is calculated as[12]

$$\langle R_h^{-1}\rangle_w = 2(\sqrt{6}/\pi)b^{-1}\int_0^\infty \mathrm{d}\beta\int_0^1 \mathrm{d}\xi\{E(\xi,\varphi)-W(\xi)\} \times (2\xi)^{-1}\left\{\frac{(1-\alpha)\bar{y}_w}{\sqrt{(1-\alpha)^2+4\alpha W(\xi)}}-(\bar{y}_w-2)\right\} \tag{27}$$

in terms of a new variable:

$$\xi = \theta_1(1-\alpha+\alpha u) \tag{28}$$

Here the enumeration gf (equation (5)) in terms of ξ is given as

$$E(\xi_1\varphi) = \mathscr{B}(\xi,\varphi) + \frac{\alpha\varphi[\mathscr{B}(\xi,\varphi)]^2}{\left[\dfrac{2\alpha W(\xi)}{-(1-\alpha+\sqrt{(1-\alpha)^2+4\alpha W(\xi)}}\right]^2-\alpha\varphi[\mathscr{B}(\xi,\varphi)-W(\xi)]} \tag{29}$$

with

$$\mathscr{B}(\xi,\varphi) = \frac{1+\varphi}{1-\varphi}W(\xi) - \frac{2\varphi}{(1-\varphi)^2\bar{y}_n}[N(\xi)-N(\varphi\xi)] \tag{30}$$

$W(\xi)$ and $N(\xi)$ are the weight fraction and the number fraction gf's of the primary chains, and are interconnected through equation (16). (See slso Table I of ref. 11.) *Figure 2*

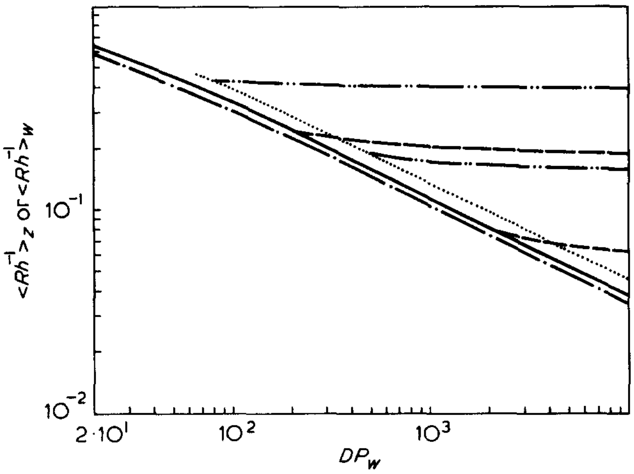

Figure 2 Reciprocal effective hydrodynamic radii plotted against the weight-average degree of polymerization. (———); the z-average reciprocal hydrodynamic radius for linear and randomly crosslinked monodisperse primary chains. (—·—·—); the z-average reciprocal hydrodynamic radius for linear and randomly crosslinked primary chains of most probable distribution. (— — — —); the weight-average reciprocal hydrodynamic radius for randomly crosslinked monodisperse primary chains where the degrees of polymerization of primary chains are 100 and 2000 respectively (from top). (—··—··—); the weight-average reciprocal hydrodynamic radius for randomly crosslinked primary chains of most probable distribution where the weight-average degrees of polymerization of primary chains are 80 and 500 respectively (from top), and (······) denotes the weight-average hydrodynamic radius for the corresponding linear chain

illustrates the computed results where the z-average reciprocal effective radius is approximately proportional to $DP_w^{-1/2}$ regardless of crosslinking while its weight-average is less dependent on DP_w due to broad polydispersity. For higher degree of polymerization, $\langle R_h^{-1}\rangle_z$ is approximated by

$$b\langle R_h^{-1}\rangle_z = 3.685(DP_w)^{-1/2} \tag{31}$$

for monodisperse primary chain distribution, or

$$b\langle R_h^{-1}\rangle_z = 3.464(DP_w)^{-1/2} \tag{32}$$

for the most probable (Schulz–Flory) primary chain distribution, as expected from the corresponding formulae for linear chains[9,14]. $\langle R_h^{-1}\rangle_w$ is rather dependent on the number-average degree of polymerization where the following approximations are valid:

$$E(\theta_1,\varphi) = \theta_1\sum m_y B_0(\varphi;y)(1-\alpha+\alpha u)^y + \frac{\alpha\varphi\theta_1^2[\sum m_y B_0(\varphi;y)(1-\alpha+\alpha u)^{y-1}]^2}{1-\alpha\varphi\theta_1[\sum m_y\{B_0(\varphi;y)-1\}(1-\alpha+\alpha u)^{y-2}]} \tag{37}$$

with

$$u = \theta_1\sum m_y(1-\alpha+\alpha u)^{y-1} \tag{38}$$

where the auxiliary variable θ_1 now carries the genetic information on the number of primary chains. The path function $\varphi(n)$ in equation (36) is set as

$$\varphi(n) = \varphi^n \tag{39}$$

where φ is to be regarded as an auxiliary variable with respect to the number of distinct paths. The method of Lagrange's expansion[15,16] applies to equation (37) which is then expressed in terms of u as

$$E(u,\varphi) = \frac{u\sum m_y B_0(\varphi;y)(1-\alpha+\alpha u)^y}{\sum m_y(1-\alpha+\alpha u)^{y-1}} + \frac{\alpha\varphi u^2[\sum m_y B_0(\varphi;y)(1-\alpha+\alpha u)^{y-1}]^2}{[\sum m_y(1-\alpha+\alpha u)^{y-1}]^2-\alpha\varphi u[\sum m_y(1-\alpha+\alpha u)^{y-1}][\sum m_y\{B_0(\varphi;y)-1(1-\alpha+\alpha u)^{y-2}]} \tag{40}$$

$$b\langle R_h^{-1}\rangle_w = 3.685(DP_n)^{-1/2} \tag{33}$$

for monodisperse primary chain distribution, or

$$b\langle R_h^{-1}\rangle_w = 2.877(DP_n)^{-1/2} \tag{34}$$

for the most probable (Schulz–Flory) primary chain distribution.

PROPERTIES OF MONODISPERSE FRACTION

The pwgf is understood as

$$u_0(\{\theta\}) = \sum_{x,k} w_{xk}x^{-1}\theta_1^x\theta_2^{\sum_n(2N_{nxk}\varphi(n))} \tag{35}$$

so that the coefficient of θ_1^x in $[\partial u_0(\{\theta\})/\partial\theta_2]_{\theta_2=1}$ yields the average of a statistical quantity $\varphi(n)$ over all x-mer isomers in the system:

$$\mathscr{C}(\theta_1{}^x)\left[\frac{\partial}{\partial\theta_2}\left\{u_0(\{\theta\})\right\}\right]_{\theta_2=1} = \sum_h w_{xk}\sum_n(2N_{nxk}\varphi(n))/x \tag{36}$$

Here w_{xk} denotes the weight fraction of the k-th isomers among x-mers, N_{nxk} the number of distinct paths of n links, and $\varphi(n)$ an arbitrary function of the path of n links. The present system consists of the primary chains crosslinked to a higher degree of polymerization, so that the x-mer fraction here is more conveniently redefined with respect to the number of primary chains rather than the degree of polymerization in order to deal with the system in systematic manner. The enumeration gf (see equation (14)) is rewritten in this context as

Thus,

$$\sum_h w_{kx}\sum_n(2N_{nxk}\varphi^n) = \frac{1}{(x-1)!}\frac{\alpha^{x-1}}{\alpha u^{x-1}}\left[E'(u,\varphi)\left\{\sum m_y(1-\alpha+\alpha u^{y-1}\right\}^x\right]_{u=0} \tag{41}$$

with $E'(u,\varphi)$ denoting $\partial E(u,\varphi)/\partial u$. When the primary chain distribution is not extremely broad, the terms $(1-\alpha+\alpha u)^{y-1}$ may be truncated from the right side of equation (40) which then reduces to

$$E(u,\varphi) = u(1-\alpha+\alpha u)\bar{f}_w(\varphi) + \frac{\alpha u^2(1-\alpha+\alpha u)\varphi\{\bar{f}_w(\varphi)\}^2}{(1-\alpha+\alpha u)-\alpha u\varphi(\bar{f}_w(\varphi)-1)} \tag{42}$$

where $\bar{f}_w(\varphi)$ is given by equation (14). It follows from equation (41), coupled with the weight fraction gf for primary chain (equation (16)), that

$$\sum_k w_{xk}\sum(2N_{nxk}\varphi^n) = \frac{1}{(x-1)!}\frac{\alpha^{x-1}}{\alpha u^{x-1}}\left[\left\{\frac{W(1-\alpha+\alpha u)}{1-\alpha+\alpha u}\right\}^x \times\left\{(1-\alpha+2\alpha u)\bar{f}_w(\varphi)+\frac{2u\alpha(1-\alpha+\alpha u)\varphi\bar{f}_w(\varphi)}{(1-\alpha+\alpha u)-\alpha u\varphi(\bar{f}_w(\varphi)-1)} + \frac{u^2\alpha^2(1-\alpha)\varphi^2(\bar{f}_w(\varphi)-1)\bar{f}_w(\varphi)}{[(1-\alpha+\alpha u)-\alpha u\varphi(\bar{f}_w(\varphi)-1)]^2}\right\}\right]_{u=0}$$

$$=\frac{1}{(x-1)!}\frac{\alpha^{x-1}}{\alpha u^{x-1}}\left[\left\{\frac{W(1-\alpha+\alpha u)}{1-\alpha+\alpha u}\right\}^{x}\right.$$

$$\times\left\{(1-\alpha+2\alpha u)\bar{f}_w(\varphi)+\alpha\bar{f}_w(\varphi)\right.$$

$$\left.\left.\sum_{n=0}^{\infty}\left[\frac{(\bar{f}_w(\varphi)-1)\alpha u}{1-\alpha+\alpha u}\right]^{n}\left[2u+\frac{n(1-\alpha)u}{1-\alpha+\alpha u}\right]\varphi^{n+1}\right\}\right]_{u=0} \tag{43}$$

Here the weight fraction gf for the primary chain is given as

$$W(\varphi)=\varphi^{y} \tag{44}$$

for monodisperse chain, or, for example

$$W(\varphi)=\varphi/[\bar{y}_n-(\bar{y}_n-1)\varphi]^2 \tag{45}$$

for a Schulz–Flory distribution.

The following calculations are confined to the system of monodisperse primary chains which will find direct applications in succeeding publications. For this system, equation (43) yields:

$$\langle\sum_{n}(2N_{nxk}\varphi^{n})\rangle_{iso}\equiv\sum_{h}w_k\sum(2N_{nxk}\varphi^{n})$$

$$=\frac{x\bar{f}_w(\varphi)}{[(y-1)x]!}\left\{[(y-1)x]!y\right.$$

$$+(x-1)!\bar{f}_w(\varphi)\sum_{n=0}^{x-2}(\bar{f}_w(\varphi)-1)^{n}\varphi^{n+1}$$

$$\left.\times\frac{[(y-1)x-(h+l)]!}{(x-n-2)!}\{n(y-2)+2(y-1)\}\right. \tag{46}$$

Here $\langle\ \rangle_{\mathrm{iso}}$ denotes the average over the statistical mixture of isomers. The weight fraction of x-mers (i.e., the degree of polymerization $=xy$) is found from the coefficient of φ in equation (46), and yields equation (47) when $xy \gg 1$:

$$w_x=\frac{(yx-x)!}{(yx-2x+2)!}\alpha^{x-1}(1-\alpha)^{(y-2)x+2} \tag{47}$$

since the sunber of the distinct paths of length 1 in the k-th x-mer is given by

$$N_{1xk}=xy-1 \tag{48}$$

The particle scattering factor is obtained for a Gaussian chain from equation (46) as

$$P(q)=\frac{\bar{f}_w(\varphi)}{xy^2[(y-1)x]!}\left\{[(y-1)x]!y\right.$$

$$+(x-1)!\bar{f}_w(\varphi)\sum_{n=0}^{x-2}(\bar{f}_w(\varphi)-1)^{n}\varphi^{n+1}$$

$$\left.\frac{[(y-1)x-(n+1]!}{(x-n-2)!}\{n(y-2)+2(y-1)\}\right. \tag{49}$$

where φ and q are defined respectively by equations (9) and (12). The radius of gyration is found from $(b^2/2)(\partial P(q)/\partial\varphi)_{\phi=1}$ so that

$$b^{-2}\langle S^2\rangle=\frac{y}{6x}\left[1+\frac{(x-1)!}{[(y-1)x]!}\sum_{n=0}^{x-2}(n+2)(y-1)^{n}\right.$$

$$\left.\times\frac{[(y-1)x-(n+1)]!}{(x-n-2)!}\{n(y-2)+2(y-1)\}\right] \tag{50}$$

which reduces for large x (number of primary chains) to

$$b^{-2}\langle S^2\rangle=\frac{y}{6x}[1+1.232(x-1)x^{1/2}] \tag{51}$$

Equation (51) suggests that the mean-square radius of gyration is proportional to the square-root of the number of primary chains when normalized by the degree of polymerization of the primary chain, i.e.,

$$\langle S^2\rangle/y\propto x^{1/2} \tag{52}$$

The experience in the preceding section demonstrates that the effective hydrodynamic radius is given by

$$(xy)^2b\langle R_h{}^{-1}\rangle_{\mathrm{iso}}=2(\sqrt{6}/\pi)\int_0^{\infty}\mathrm{d}\beta\langle\sum 2N_{nxk}\varphi^{n})\rangle_{\mathrm{iso}} \tag{53}$$

with φ^n defined by equation (26), so that

$$(xy)^2b\langle R_h{}^{-1}\rangle_{\mathrm{iso}}=2(\sqrt{6}/\pi)\int_0^{\infty}\frac{x(\bar{f}_w(\varphi)-1)}{[(y-1)x]!}\left[[(y-1)x]!^{y}\right.$$

$$+(x-1)!\bar{f}_w(\varphi)\sum_{n=0}^{x-2}(\bar{f}_w(\varphi)-1)^{n}\varphi^{n+1}$$

$$\left.\frac{[(y-1)x-(n+1)]!}{(x-n-2)!}\{n(y-2)+2(y-1)\}\right]\mathrm{d}\beta \tag{54}$$

which reduces for large x (number of primary chains) to

$$b\langle R_h{}^{-1}\rangle\cong\frac{3.685}{xy^{1/2}}(1+0.6765(x-1)x^{-1/4}) \tag{55}$$

Equation (55) suggests that the effective hydrodynamic radius is inversely proportional to the square-root of the number of primary chains when normalized by the square-root of the degree of polymerization, i.e.,

$$\langle R_h{}^{-1}\rangle y^{1/2}\propto x^{-1/4} \tag{56}$$

The computed results for the particle scattering factors are shown in *Figures 3* and *4* where the maxima in the Kratky plots as well as the initial upturn in the Zimm plots are more pronounced with increasing degree of crosslinking. Equations (51) and (55) for the radius of gyration and the reciprocal effective hydrodynamic radius, respectively, are nearly exact over a whole range of x (the number of primary chains) as seen from *Figure 5* where only a minor deviation is observed at the smaller x values.

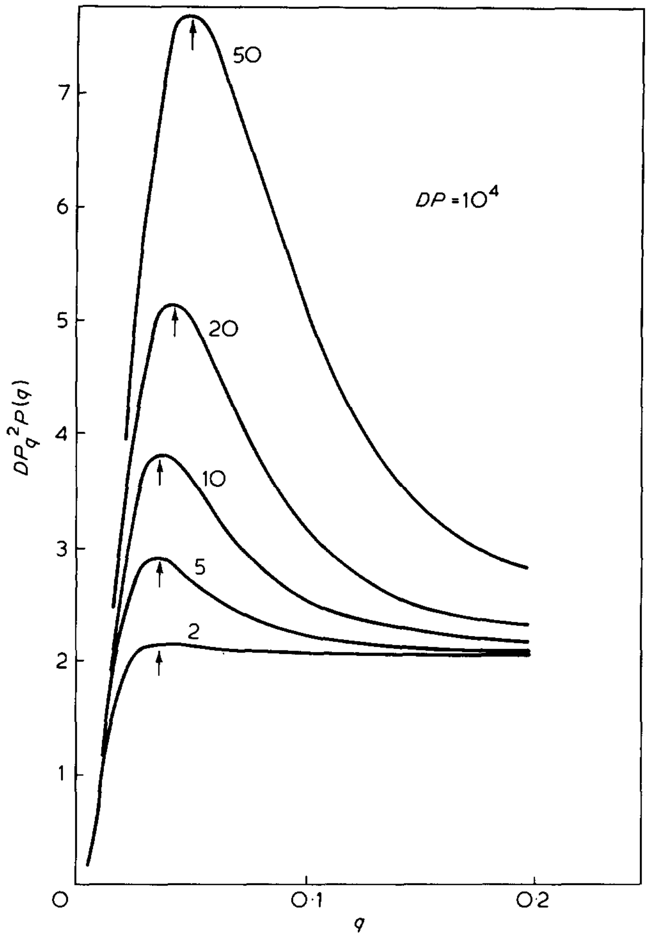

Figure 3 Kratky plots of monodisperse fractions from the randomly crosslinked monodisperse primary chains. Each number in the figure denotes the number of primary chains (i.e., the number of cross-links + 1), and $q = (4\pi/\lambda)\sin(\nu/2)$

The ρ ratio, a dimensionless quantity defined by[17]

$$\rho \equiv \langle R_h^{-1}\rangle_z \langle S^2\rangle_z^{1/2} \tag{57}$$

decreases from 1.504[5] (for the crosslinked system with monodisperse primary chain distribution) or 1.732 (for the crosslinked system with most probable primary chain distribution) to 1.130 by fractionation. (This value, 1.130, is expected to be slightly larger for the fraction from the system with broader primary chain distribution.) *Table 1* shows the ρ ratio as a function of x. The random crosslinking proceeds so as to cancel the effect of crosslinking on the ρ ratio with polydispersity.

DYNAMIC STRUCTURE FACTOR

The useful information on branching density/type and polydispersity is also provided from the first cumulant Γ (initial logarithmic derivative) of the dynamic structure factor which is given as[18]

$$\Gamma/q^2 \equiv D_{\mathrm{app}}(q) = \sum_n \varphi_n{}^{\varrho}/x^2 P(q) \tag{58}$$

for the monodisperse system, or

$$\Gamma_z/q^2 \equiv D_{z,\mathrm{app}}(q) = \sum_{x,n} w_x x^{-1} \varphi_n{}^{\varrho}/DP_w P_z(q) \tag{59}$$

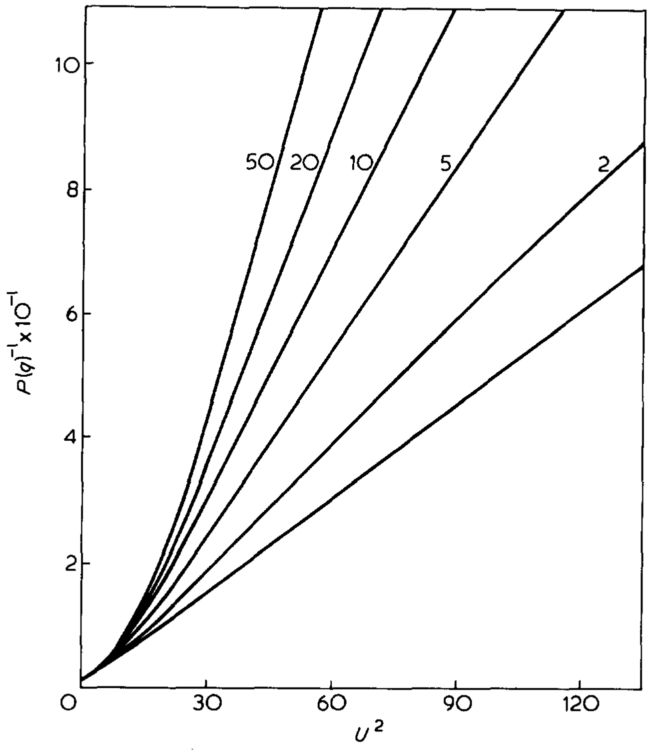

Figure 4 Zimm plots of *Figure 2* where $U^2 = q^2\langle S^2\rangle$. The solid straight line shows slope 1/3

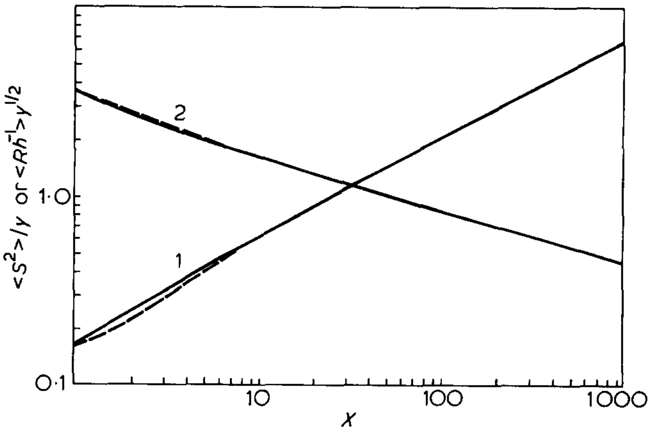

Figure 5 Normalized radius of gyration (Curve 1) and the normalized reciprocal effective hydrodynamic radius (Curve 2) plotted against the number of primary chains x (i.e., the number of cross-links + 1). The broken lines denote the respective approximations by equations (51) and (55)

Table 1 ρ Ratio for monodisperse fraction from crosslinked monodisperse primary chains

x	From equations (51) and (55)	Exact
1	1.5044	–
2	1.3819	1.3748
3	1.3746	–
4	1.3265	1.3144
6	1.2979	–
8	1.2784	1.2614
10	1.2638	1.2480
20	1.2239	1.2135
40	1.1932	1.1878
80	1.1712	1.1693
100	1.1657	1.1318

in terms of the observable z-average for the polydisperse system where the free draining term is subtracted. The non-preaveraged Oseen interaction term $\varphi_n{}^Q$ is approximated by the sum of two terms; the preaveraged Oseen interaction term and its correction. Thus

$$\varphi_n{}^Q \simeq \varphi_{n,\mathrm{pre}}{}^Q + \Delta\varphi_n \tag{60}$$

where

$$\varphi_{n,\mathrm{pre}}{}^Q = An^{-1/2}\exp(-nt) \tag{61}$$

$$\Delta\varphi_n = \tfrac{1}{5}An^{1/2}t^2\exp(-na^2t^2) \tag{62}$$

with

$$A = k_BT/(6^{1/2\ 3/2}b_0) \tag{63}$$

$$t^2 = b^2q^2/6 \tag{64}$$

$$a^2 = 0.72 \tag{65}$$

(The notations used here closely follow those in ref. 18.) Thus the first cumulant derived analogously to the derivation of equation (25) or (54) is

$$(DP_wP_z(q))D_{z,\mathrm{app}}(q) =$$

$$\frac{2}{\sqrt{\pi}}A\int_0^\infty \mathrm{d}\beta\{(1+\alpha\varphi_1)\bar{f}_w(\varphi_1)/[1-\alpha\varphi_1(\bar{f}_w(\varphi_1)-1)]-1\}$$

$$+\frac{At^2}{5\sqrt{\pi}}\int_0 \frac{\mathrm{d}\beta}{\beta^2}\left\{\frac{(1+\alpha\varphi_2)\bar{f}_w(\varphi_2)}{1-\alpha\varphi_2(\bar{f}_w(\varphi_2)-1)}-\frac{(1+\alpha\varphi_3)\bar{f}_w(\varphi_3)}{1-\alpha\varphi_3(\bar{f}_w(\varphi_3)-1)}\right\} \tag{66}$$

for a whole ensemble of the randomly crosslinked system, or

$$(xy)^2P(q)D_{\mathrm{app}}(q) = \frac{2}{\sqrt{\pi}}A\int_0^\infty \mathrm{d}\beta\left[\frac{x(\bar{f}_w(\varphi_1)-1}{[(y-1x]!}\left\{[(y-1)x]!y\right.\right.$$

$$+(x-1)!\bar{f}_w(\varphi_1)\sum_{n=0}^{x-2}(\bar{f}_w(\varphi)-1)^n\varphi_1{}^{n+1}$$

$$\left.\left.\times\frac{[(y-1)x-(n+1)]!}{(x-n-2)!}\{n(y-1)+2(y-1)\}\right\}\right]$$

$$+\frac{At^2}{5\sqrt{\pi}}\int_0^\infty\frac{\mathrm{d}\beta}{\beta^2}\left[\frac{x\bar{f}_w(\varphi_2)}{[(y-1)x]!}\left\{(y-1)x]!\,y+(x-1)!\bar{f}_w(\varphi_2)\right.\right.$$

$$\left.\times\sum_{n=0}^{x-2}(\bar{f}_w(\varphi_2)-1)\varphi_2{}^{n+1}\frac{[(y-1)x-(n+1)]!}{(x-n-2)!}\{n(y-2)+2(y-1)\}\right\}$$

$$-\frac{x\bar{f}_w(\varphi_3)}{[(y-1)x]!}\left\{[(y-1)x]!\,y+(x-1)!\bar{f}_w(\varphi_3)\times\sum_{n=0}^{x-2}(\bar{f}_w(\varphi_3)-1)^n\varphi_3{}^{n+1}\right.$$

$$\left.\left.\times\frac{[(y-1)x-(n+1)]!}{(x-n-2)!}\{n(y-2)+2(y-1)\}\right\}\right] \tag{67}$$

for its monodisperse fraction, with

$$\left.\begin{aligned}\varphi_1 &= \exp(-\beta^2-t^2)\\ \varphi_2 &= \exp(-a^2t^2)\\ \varphi_3 &= \exp(-\beta^2-a^2t^2)\end{aligned}\right\} \tag{68}$$

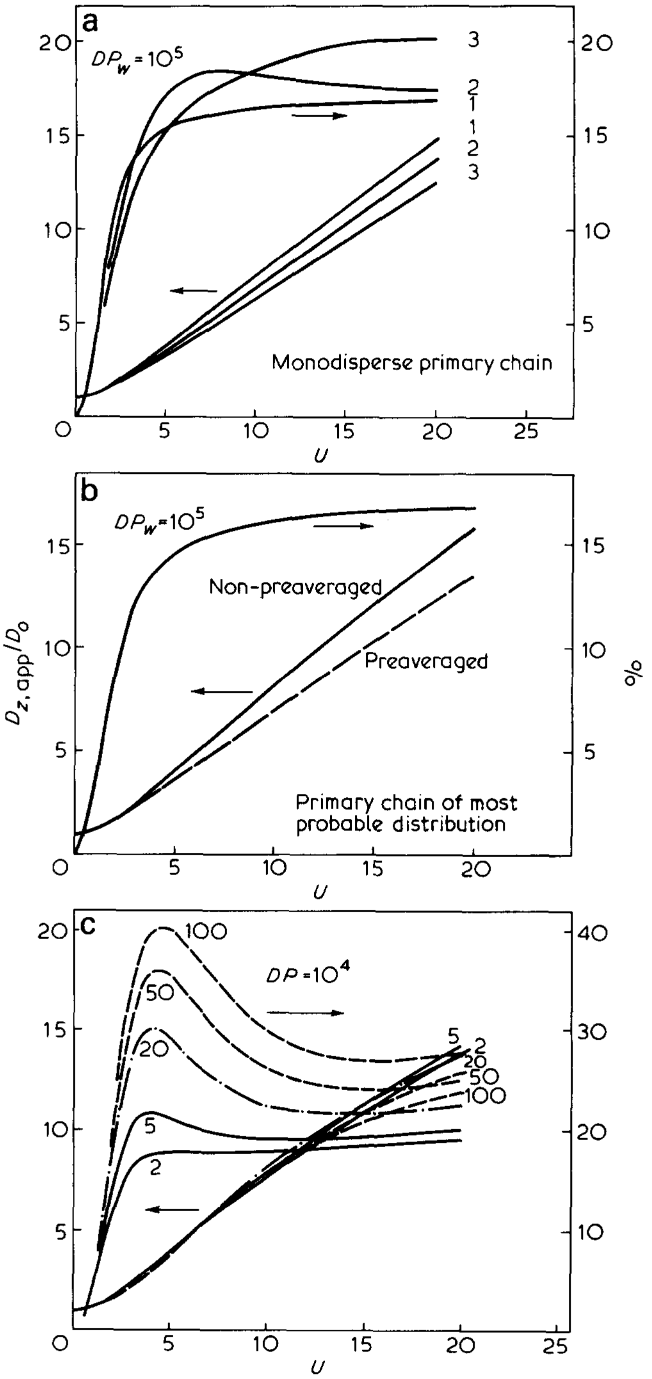

Figure 6 The normalized first cumulants D_{app}/D_0 and the relative % error by preaverage approximation plotted against U $(=q\langle S^2\rangle^{1/2})$. D_{app} and $\langle S^2\rangle$ for polydisperse systems correspond to their respective z-averages (observables). (a) Curve 1; monodisperse linear chain, Curve 2; crosslinked monodisperse primary chains of $y = 10^4$, and Curve 3; crosslinked monodisperse primary chains of $y = 10^3$. (b) Linear and crosslinked primary chains of most probable distribution. (c) Monodisperse fractions from crosslinked monodisperse primary chains where each number in the figure denotes the number of primary chains (i.e., the number of crosslinks + 1)

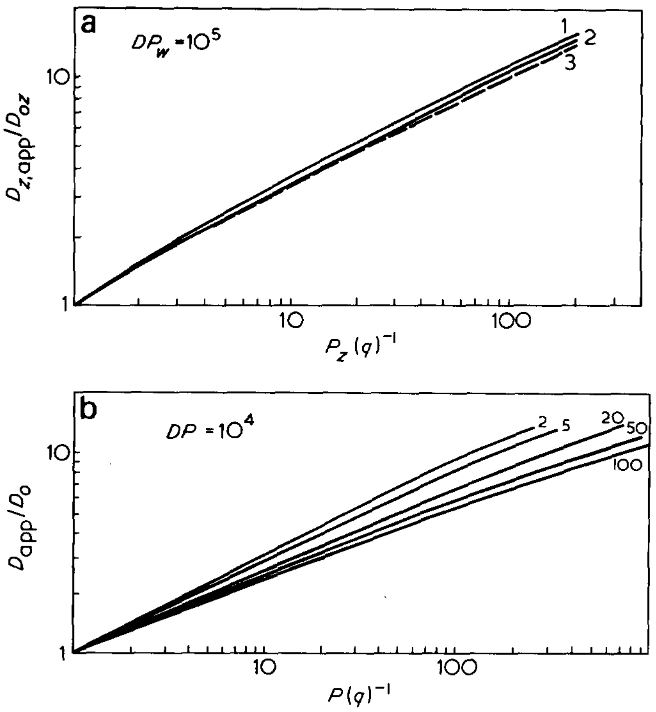

Figure 7 Normalized frist cumulants plotted against the reciprocal particle scattering factor. (a) Linear and crosslinked primary chains of most probable distribution (Curve 1), linear monodisperse chain (Curve 2), and crosslinked monodisperse primary chains of $y = 10^4$ (Curve 3). (b) Monodisperse fractions of crosslinked monodisperse primary chains where each number in the figure denotes the number of primary chains (i.e., the number of crosslinks + 1)

$\bar{f}_w(\varphi)$ is as defined in equation (13). The particle scattering factor $P_z(q)$ or $P(q)$ is given by equation (10) or (49), respectively.

The computed results are shown in *Figure 6* where the normalized first cumulants D_{app}/D_0 are plotted against U $(=\langle S^2\rangle^{1/2}q)$ as well as the relative error by preaverage approximation. The randomly crosslinked system with most probable primary chain distribution exhibits no change on the angular dependence of the first cumulant regardless of crosslinking. In the randomly crosslinked system with monodisperse primary chain distribution, this angular dependent curve bends down slightly more with crosslinking though its initial slope remains unchanged. The situation becomes clear when plotted as the normalized first cumulant against the reciprocal particle scattering factors (*Figure 7*) where the initial slope is estimated as 0.6 or 0.52, respectively, for the randomly crosslinked system with most probable or monodisperse primary chain distribution in accordance with the results of Burchard *et al.*[18] This slope is even smaller with an increasing number of primary chains (i.e., the number of crosslinks) in the monodisperse fraction (*Figure 7*) where the curves are slightly S-shaped, and the relative error by preaverage approximation reveals its characteristic maxima as observed for star-shaped molecules.

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