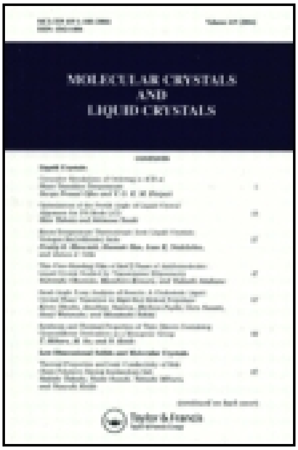

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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Version of record first published: 13 Dec 2006.

To cite this article: Milko Matey & Paskal Kartalov (1987): Changes in the Cross-Linking Density of Three-Dimensional Macromolecular Networks, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 152:1, 383-392

To link to this article: http://dx.doi.org/10.1080/00268948708070968

Mol. Cryst. Liq. Cryst., 1987, Vol. 152 pp. 383-392
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Printed in the United States of America

CHANGES IN THE CROSS-LINKING DENSITY OF THREE-DIMENSIONAL MACROMOLECULAR NETWORKS

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Abstract Equations are suggested for the strand concentration in three-dimensional macromolecular networks and for their number-average molecular weight. Concepts of time dependences of spatial cross-linking density have been referred to. The kinetics of physical cross-linking has been studied. Complex values are introduced for describing the frequency dependences of network strands concentration and their corresponding number-average molecular weights.

INTRODUCTION

Polymers can become cross-linked as a result of processes of synthesis or chemical modifications with cross-linkage agents. Cross-linked macromolecular chains (MMC) form spatial macromolecular networks (SMMN) with different characteristics as network chain concentration (N_c), number-average molecular weight of strands ($\langle M_{n,c} \rangle$), different topological features (entanglements, MMC meshing) etc.[1] After the chemical processes of MMC cross-linking have ceased, the values N_c and $\langle M_{n,c} \rangle$ are considered as constants.[1-3] When examining the viscoelastic behaviour of chemically non-cross linked polymers which are in a rubbery state it is assumed that SMMN are unstable and fluctuating.[1-5] In these SMMN macromolecular chains cross-link by means of physical bonds (entanglements, mechanical meshing, intermolecular forces of interaction) of kinetic nature.[6] As a result of examining the behaviour of MMN of polymers in a rubbery state and explaining the deviations of viscoelastic functions from the type which ensues from the linear kinetic theory of viscoelasticity discussed in a previous paper,[7] an equation has been suggested for the temperature dependence of $N_c = f(T)$.

The purpose of this work is to work out equations for the time and frequency dependence of network chain concentration $N_c = f(t,f)$ and the number-average molecular weights of strands $\langle M_{n,c} \rangle = f(t,f)$.

THEORETICAL RESULTS AND DISCUSSION

At the formation of three-dimensional macromolecular networks strand concentration (N_c) is a sum of the concentrations of network chains, confined within the chemical cross-link bonds ($N_{c,ch}$) and the physical links ($N_{c,ph}$),

$$N_c = N_{c,ch} + N_{c,ph} \, . \tag{1}$$

When there are different kinds of chemical and physical network bonds, the corresponding strand concentration will be given by the following expression:

$$N_c = \sum_i N_{c,ch,i} + \sum_i N_{c,ph,i} \quad (2)$$

According to the suggested hypothesis [8] for the time dependence of N_c, equation (2) takes the form

$$N_c(t) = N_{c,ch}(t) + N_{c,ph}(t) = \sum_i N_{c,ch,i}(t) + \sum_i N_{c,ph,i}(t) \; . \quad (3)$$

If no mechanochemical, radiation chemical, oxidation-destructive, vulcanization and other processes take place, $N_{c,ch}(t)$ = const. and equation (3) takes the form

$$N_c(t) = N_{c,ch} + N_{c,ph}(t) = N_{c,ch} + \sum_i N_{c,ph,i}(t). \quad (4)$$

Upon chemical cross-linking of MMC, part of the physical bonds become trapped,[9-13] the probability for this phenomenon to occur being T_c. The physical bonds trapped in the course of chemical cross-linking cannot be destroyed and the following expression is valid for $N_{c,ph}(t)$

$$N_{c,ph}(t) = \sum_i T_{c,i} N_{c,ph,i} + \sum_i (1 - T_{c,i}) N_{c,ph,i}(t) \; . \quad (5)$$

The concrete form of the time dependences $N_{c,ph}(t)$ will depend on the type of outside impacts causing structural relaxation of three-dimensional macromolecular networks[14,15]. After final relaxation of the macromolecular structure, three-dimensional networks will have an equilibrium value of strand concentration ($N_{c,e}$)

$$N_{c,e} = \lim_{t \to \infty} N_c(t) = N_{c,ch} + \sum_i T_{c,i} N_{c,ph,i} =$$

$$N_{c,ch} + N_{c,ph,e} , \qquad (6)$$

where $N_{c,ph,e}$ is the equilibrium density of spatial physical cross-linking (the concentration of network chains confined within the physical bonds).[16]

Upon macromolecular structural relaxation, the non-trapped physical links of the network are destroyed with time and form new links which are ineffective in relation to the given outside impact, since they are not under strain.

In the general case, besides on time (t), $N_{c,ph}$ will depend also on temperature[7], on the magnitude of the corresponding type of sample relative deformation (e_r), the polymer volumetric part in the swelled gel (V_r), the hydrostatic pressure(P).

$$N_{c,ph} = F(t, T, e_r, V_r, P) \qquad (7)$$

Since N_c is an integral characteristic giving the strand concentration, average molecular weights of strands ($M_{j,c}$) have to be determined for the structural microheterogeneity of three-dimensional networks

$$\langle M_{j,c} \rangle = \left[\sum_i N_{c,i} M_{c,i}^{j}\right] / \left[\sum_i N_{c,i} M_{c,i}^{j-1}\right], j=1,2\ldots \qquad (8)$$

where $M_{c,i}$ is the molecular weight of the i strand of three-dimensional network.

At j = 1, from equation (8) we obtain the

the formula for the number-average molecular weight ($\langle M_{n,c} \rangle$) of three-dimensional MMN chains; at $j = 2$ - the weight-average molecular weight ($\langle M_{w,c} \rangle$); at $j = 3$ - the Z-average molecular weight ($\langle M_{z,c} \rangle$) and so on.

As the relation between N_c, $\langle M_{n,c} \rangle$ and polymer density (d_p) is expressed by the equation

$$N_c \langle M_{n,c} \rangle = d_p \,, \tag{9}$$

when there exist time dependences $N_c(t)$ and $\langle M_{n,c}(t) \rangle$, according to equation (4) we obtain

$$\frac{d_p}{\langle M_{n,c}(t) \rangle} = N_c(t) = N_{c,ch} + N_{c,ph}(t) \,. \tag{10}$$

Upon relaxation of macromolecular structure as a result of labile physical bond destruction, $\langle M_{n,c}(t) \rangle$ will tend to the equilibrium value $\langle M_{n,c,e} \rangle$, i.e.

$$\lim_{t \to \infty} \langle M_{n,c}(t) \rangle = \langle M_{n,c,e} \rangle = \text{const.} \tag{11}$$

From equations (6), (10) and (11) we derive the following equation for $\langle M_{n,c,e} \rangle$

$$\langle M_{n,c,e} \rangle = \frac{d_p}{N_{c,ch} + N_{c,ph,e}} = \frac{d_p}{N_{c,e}} \,. \tag{12}$$

From equations (4), (5), (10) and (12) we obtain the following expression for the time dependence $\langle M_{n,c}(t) \rangle$

$$\langle M_{n,c}(t) \rangle = \left[\frac{1}{d_p} \sum_i (1 - T_{c,i}) N_{c,ph,i}(t) + \frac{1}{\langle M_{n,c,e} \rangle} \right]^{-1} . \tag{13}$$

The magnitude of $\langle M_{n,c,e}\rangle$ can be experimentally established by determining the equilibrium static modulus of torsion (G_e)[17].

$$G_e = \frac{gd_pRT}{\langle M_{n,c}\rangle}\frac{\langle r_c^2\rangle}{\langle r_f^2\rangle}\quad 1 - \frac{2\langle M_{n,c,e}\rangle}{\langle M_{n,o}\rangle}\quad , \qquad (14)$$

where g is a front-factor, giving the energy difference between trans- and gosh-conformations; R - the gas constant, $\langle r_c^2\rangle$ is the mean quadratic length of the end-to-end distance vector in three-dimensional macromolecular networks; $\langle r_f^2\rangle$ is the mean quadratic length of network chains, provided they are not strained; $\langle M_{n,o}\rangle$ is the number-average molecular weight of the non-cross-linked polymer.

After substituting equation (14) in equation (13), we obtain the following for time dependence $\langle M_{n,c}(t)\rangle$

$$\langle M_{n,c}(t)\rangle = \left[\frac{1}{d_p}\sum_i(1-T_{e,i})N_{c,ph,i}(t) + \frac{G_e}{gd_pRT}\left(\frac{\langle r_c^2\rangle}{\langle r_f^2\rangle}\right)^{-1} + \frac{2}{\langle M_{n,o}\rangle}\right] . \qquad (15)$$

In general, the following equation is valid for $\langle M_{n,c}\rangle$

$$\langle M_{n,c}\rangle = F(t,T,e_r,\ V_r,P)\ . \qquad (16)$$

As the term $\langle r_c^2\rangle/\langle r_f^2\rangle \approx 1$[18] and at high cross-linking densities $1 - 2\langle M_{n,c,e}\rangle/\langle M_{n,o}\rangle = 1$, after substituting equation (9) in equation (14) we obtain the following

$$G_e = gN_cRT\ . \qquad (17)$$

By applying dynamo-mechanical treatments, the complex modulus $G^* = G' + iG''$ has been determined (G' - storage modulus, G'' - loss modulus, $i^2 = -1$).[1] At low frequencies (f) $|G^*|$ with cross-linked polymers in a rubbery state is close to G_e in magnitude, i.e.

$$\lim_{f \to 0} G^*(f) = G_e \ . \qquad (18)$$

There being a dependence of strand concentration on frequency (f), the following complex quantity can be introduced for describing the viscoelastic behaviour of cross-linked polymers

$$N_c^*(f) = N_c'(f) + iN_c''(f) \ , \qquad (19)$$

where $N_c'(f)$ is the storage strand concentration, determining elastic energy storage at dynamic treatment of the polymer, and $N_c''(f)$ is the loss strand concentration, determining mechanical energy dissipation at cyclic deformation.

Correspondingly, equation (17) takes the following form

$$G^*(f) = gN_c^*(f)RT \ . \qquad (20)$$

Since g is a parameter that is close to 1, from equation (20) we can obtain the following expressions for $N_c'(f)$ and $N_c''(f)$

$$N_c'(f) = \mathrm{Re}N_c^*(f) = G'(f)/RT \qquad (21)$$

$$N_c''(f) = \mathrm{Im}N_c^*(f) = G''(f)/RT \ , \qquad (22)$$

and for $\mathrm{tg}b_N(f)$

$$\mathrm{tg}b_N(f) = \frac{\mathrm{Jm}N_c^*(f)}{\mathrm{Re}N_c^*(f)} = \frac{N_c''(f)}{N_c'(f)} = \frac{G''(f)}{G'(f)} =$$

$$= tgb_G(f) \ , \tag{23}$$

where $tgb_G(f)$ is the mechanical dissipation coefficient.

At low frequencies (f) $N_c^*(f)$ will tend towards the equilibrium value $N_{c,e}$, i.e.

$$\lim_{f\to 0} N_c^*(f) = N_{c,e} = G_e/RT \ . \tag{24}$$

The dependence of N_c on f determines respectively the dependence of the complex quantity, number-average molecular weight of network strands $\langle M_{n,c}\rangle$, on f

$$\langle M_{n,c}^*(f)\rangle = \frac{d_p}{N_c^*(f)} = \frac{d_p N_c'(f)}{N_c'^2(f)+N_c''^2(f)} - i\frac{d_p N_c''(f)}{N_c'^2(f)+N_c''^2(f)} = \frac{1}{1+tg^2b_G(f)}\frac{d_p}{N_c'(f)} - i\frac{1}{1+1/tg^2b(f)}\frac{d_p}{N_c''(f)} = \langle M_{n,c}'(f)\rangle - i\langle M_{n,c}''(f)\rangle \ , \tag{25}$$

where $\langle M_{n,c}'(f)\rangle$ is the number-average molecular weight of storage network chains, and $\langle M_{n,c}''(f)\rangle$ - that of loss network chains.

Accordingly, the following expression is obtained for $tg\ b_M$

$$tg\ b_M(f) = \frac{Jm\langle M_{n,c}(f)\rangle}{Re\langle M_{n,c}(f)\rangle} = \frac{\langle M_{n,c}''(f)\rangle}{\langle M_{n,c}'(f)\rangle} = \frac{N_c''(f)}{N_c(f)} = tg\ b_G \ . \tag{26}$$

In general, the following equation will be valid for $\langle M^{*}_{n,c} \rangle$

$$\langle M^{*}_{n,c} \rangle = F(f, T, e_r, V_r, P) \ . \tag{27}$$

These time /$N_c(t)$ and $\langle M_{n,c}(t) \rangle$/ and frequency /$N^{*}_c(f)$ and $\langle M^{*}_{n,c}(f) \rangle$/ dependences can be used for quantitative determination of the phenomena thixotropy, strain relaxation, relaxation transitions, etc.

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