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## EQUILIBRIUM SWELLING PROPERTIES OF LIGHTLY CROSSLINKED ISOTROPIC NETWORKS: NATURAL RUBBER CROSSLINKED IN DRY STATE

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### ABSTRACT

Lightly crosslinked natural rubber (NR) networks have been characterized by equilibrium swelling in toluene. A good agreement between the equilibrium swelling crosslink-junction densities ( $\mu_E$ ) and the values expected from the stoichiometry of dicumyl peroxide decomposition ( $\mu_c$ ) has been obtained using Flory's early equation of state. The applicable value of  $\chi = 0.37$  was found to compare equally well and is in tandem with the previously reported literature values of  $\chi = 0.391$  and  $\chi = 0.35$  from swelling and heat of mixing measurements, respectively.

At low crosslink-junction densities i.e.,  $\mu_E \leq 4.2 \text{ mM.l}^{-1}$  corresponding on average to 4 crosslink-junctions per *cis* 1,4-polyisoprene chain and below, network formation is found to be incomplete. The approach used also provides a simple way of differentiating lightly crosslinked networks from the state of gelation.

## INTRODUCTION

Equilibrium swelling measurements provide a simple route in determinations of rubber network properties. The fundamental relationships of equilibrium swelling rely on classical theories [1, 2], and the properties of polymers in solution; the latter are derived from statistical thermodynamic fundamentals [3-9]. Thus, Flory-Huggins lattice model predicts the change in free energy of mixing polymer chain and solvent at infinite dilution to be  $RT[\ln(1 - v) + v + \chi'v^2]$ ; here,  $(v)$  is the volume fraction of the polymer in solution and the enthalpic interactions with solvent molecules are expressed in terms of  $\chi'$  - the polymer-solvent interaction parameter. This parameter has a specific value dependent on the interplay of molecular forces [10] and is a thermodynamic constant at  $\lim v_0$  [11-12].

The thermodynamic equilibrium state for a swollen network is approximated taking the contribution to the change in free energy -upon mixing network and solvent equivalent to that upon mixing the polymer and solvent. At equilibrium, for networks formed in the dry state [13-18] the predictions are:

$$\ln(1 - v_r) + v_r + \chi v_r^2 = -N_E \cdot V_1 \cdot v_r^{1/3} \quad (1)$$

or

$$\ln(1 - v_r) + v_r + \chi v_r^2 = -N_E \cdot V_1 \cdot (v_r^{1/3} - v_r) \quad (2)$$

where,

$v_r$  = the equilibrium volume fraction of gel in the swollen network;

$\chi$  = the network - solvent interaction parameter;

$N_E$  = the number concentration or chain segments density between crosslink-junctions =  $\rho M_E$ ;

$M_E$  = the average molecular weight of segments between two crosslink-junctions;

$V_1$  = the molar volume of solvent;

$\rho$  = specific gravity of the network which, at low crosslink-junction concentration, approximates to that of polymer.

Equation 2 is a modification by Flory [18] that accounts for a reduced opposition of the elastic network to swelling.

Similarly, equilibrium swelling for a network designed by crosslinking in a diluent [19-21] is:

$$\ln(1 - v_r) + v_r + \chi v_r^2 = -N_E \cdot V_1 \cdot (v')^{2/3} \cdot f(v_r) \quad (3)$$

with  $v'$  = volume fraction of the polymer in diluent prior to swelling.

The above mentioned descriptions rely further on the assumption that the deformation is affine i.e., in swelling, the mean spacing of junction points maintain the proportionality with their undeformed state mean relaxed spacing. Intuitively, it is suggested that further than what the excluded volume effects do in real polymer solutions, swelling network segments remain restricted in their freedom of placement to the extent depending on the degree of crosslinking; the process of crosslinking brings closer the network chains with increasing crosslink junction densities (and decreases in specific volume).

Another case in concept is that known as the phantom model [22-24] where the junction points can fluctuate independently from what the elastic segments prevent them from doing i.e., the deformation is non-affine. This model predicts the elasticity to be proportional to  $(N_E - \mu_E)$  rather than  $N_E$ , and prescribes a swelling equilibrium of the form:

$$\ln(1 - v_r) + v_r + \chi v_r^2 = -(N_E - \mu_E) \cdot V_1 \cdot f(v_r) \quad (4)$$

where,  $\mu_E$  is the concentration of crosslink junctions.

In the tests for network theories the values of  $N_E$  or crosslink junction densities ( $\mu_E$ ) are corrected by a factor  $(1 - 2 M_E/M_n)^{-1}$  as if the loose segments of the chain ends were effectively linked to the elastic network [25].

$\chi'$ - values are found to vary with  $(v)$ , linearly [10-12] or monotonous fashions [26] perhaps with the only exception of *cis* 1,4-polyisoprenes in benzene where  $0.40 < \chi' < 0.42$  [27] for a wide range of  $(v)$ .

The variation of  $(\chi)$  with  $(v_r)$  is well established [28-33], and may be rationalized in terms of increased polymer-polymer segment interactions: that is, these interactions are somewhat pronounced near crosslink junctions as pointed out by Hermans [34], and likely to be accountable for the decreases in  $(\chi)$  that are appreciable with increase in  $(v_r)$ ; the exception perhaps is the independence of  $(\chi)$  from  $(v_r)$  for polydimethylsiloxanes in branched aliphatic hydrocarbon solvents, namely 2,3 - dimethylpentane and 2,2,4 - trimethylpentane [32].

An extensive body of experimental observations establish the primary factors influencing the swelling properties of polymer networks. The crosslink density and the magnitude of specific interactions [28] set aside, often reference is made to topological constraints: the rapidity with which crosslinks are gener-

ated is a design variable and may set networks in ways that complicate polymer segment dispositions between junctions particularly at high  $\mu$ -values. Applied techniques in crosslinking should also avoid possibilities leading to non-uniform junction distribution in the network structure.

Hypothetically, the ratio  $M_n/M_E = 2$  is the limit at which a crosslinked network exists. Below this limit, polymer chains may have been incorporated into highly branched three-dimensional non-linear structures with extensive connections to other similar dispositions [35]. Even at this limit it seems unlikely that a completely connected network is achieved in practice: given the stochastic nature of free radical reactions used in crosslinking, extents of crosslinking are expected to exceed the stage where, on average one crosslink junction per polymer occurs, in order for the network to be formed.

This work examines in detail, the applicability of the classical predictions for network swelling in equilibrium for the case of natural rubber. It is a verification exercise that had been anticipated for networks of low crosslink-junction densities and specifically explores the network behavior at low cross-link-junction densities, thus far unreported.

## EXPERIMENTAL

Natural rubber (*cis* 1,4 -polyisoprene with  $M_n = 2.2 \times 10^5$  g.mole<sup>-1</sup>) used was Standard Malaysian Rubber (SMR-L), supplied by Rubber Research Institute of Malaysia, Sungai Buloh, Selangor-Malaysia. Toluene (Analyzed-reagent grade, (J. T. Baker Inc. Phillipsburg, NJ, USA) and dicumyl peroxide-DCP (BDH, Poole, England) were used as supplied.

### Preparation and Crosslinking of Rubber Sheets

60 grams of chopped pieces of unmasticated natural rubber (NR) were dissolved in toluene so as to give a 10% w/w stock solution. The dissolution was effected on a shaker table (Gerhardt, Bonn-Germany) at 15 rpm and ambient temperature, up to 24 hours. Dicumyl peroxide (2 pphr / 4 pphr) was added into this stock solution and left to dissolve overnight.

The sheets of uncrosslinked rubber were obtained by casting the rubber from its solution by evaporation in glass-plate moulds and crosslinked in the dry state at 120°C as recommended [36] using a hot press (Fortune, Vlaardingen-Holland) at the pressure of 1.67 kg<sub>f</sub>.cm<sup>-2</sup>. The rate constant used for the decom-

TABLE 1. Expected Network Parameters Based on the Decomposition Kinetics of Dicumyl Peroxide for Natural Rubber (NR) Crosslinked in the Dry State

DCP content - time (pphr) (min)	$\mu_c$ (mM.l <sup>-1</sup> )	$N_c$ (mM.l <sup>-1</sup> )	$M_c \times 10^{-4}$ (g.mole <sup>-1</sup> )	$M_n/M_c$
2 63	9.1	18.2	5	4.4
2 77	11.0	22.0	4.2	5.2
2 99	13.8	27.6	3.3	6.7
4 56	16.4	32.8	2.8	7.9
4 66	19.1	38.2	2.4	9.2
4 77	22.0	44.0	2.1	10.5
4 87	24.2	48.4	1.9	11.6
4 99	26.7	53.4	1.7	12.9
4 110	29.2	58.4	1.6	13.8

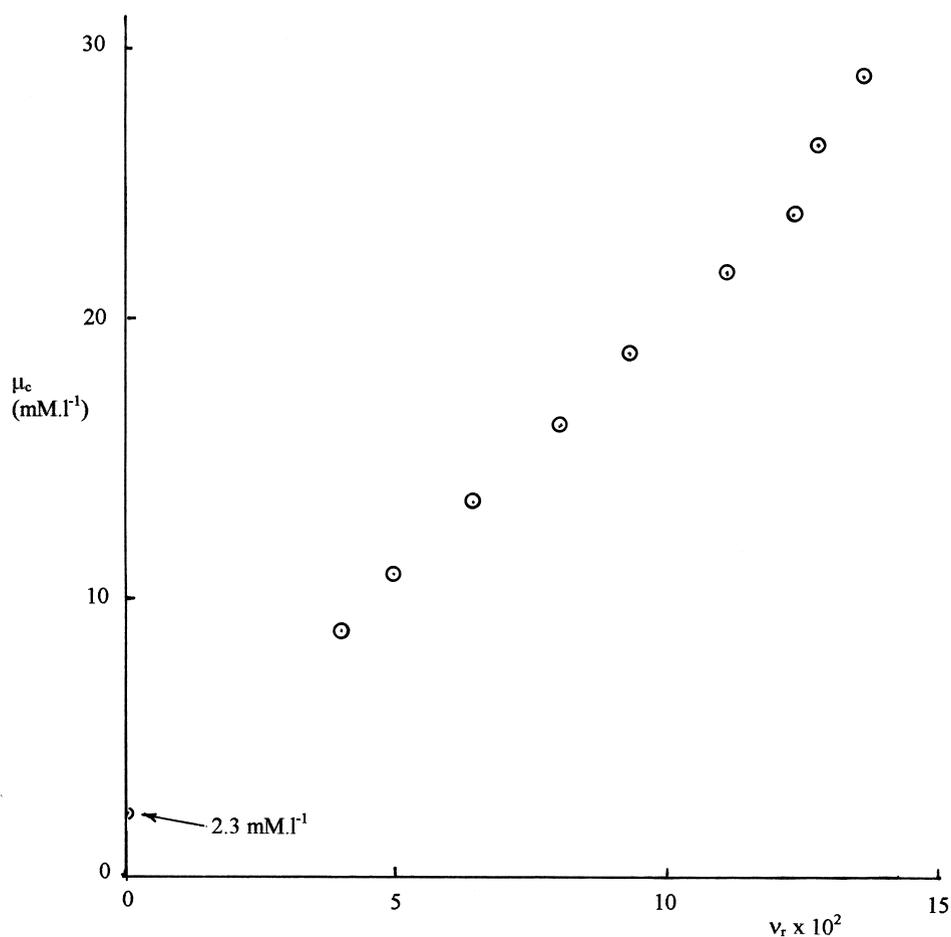
position of dicumyl peroxide at 120°C  $k_d = 3.835 \times 10^{-5} \text{ sec}^{-1}$  differed from a reported value [36] by 1%.

For a series of sheets containing the peroxide, the time under the hot press was varied so as to obtain specimens of varying crosslink-junctions densities. Naturally occurring antioxidants, metallic impurities and reducing amines are considered not to affect the course of the crosslinking reactions.

The thicknesses of the sheets were kept low, between 0.6 mm and 0.8 mm to avoid anisotropy of crosslinking. Chemical crosslink-junction densities ( $\mu_c$ ), from the decomposition kinetics of dicumyl peroxide [37-39] -and the corresponding values for the average molecular weights between crosslink-junctions ( $M_c$ ) as well as average elastic segment densities ( $N_E$ ) are given in Table 1.

### Determination of $v_r$

0.20 g-0.30 g specimens of networks were left to swell in toluene at 25°C  $\pm 1^\circ\text{C}$ . A plateau value of swelling was reached within 6 hours. The equilibrium volume fractions of the swollen samples ( $v_r$ ) were determined gravimetrically assuming volume additivity of components with the specific gravity of rubber  $\rho_{NR} = 0.916 \text{ g cm}^{-3}$ , that of toluene =  $0.865 \text{ g cm}^{-3}$ , and molar volume of toluene  $V_1 = 106.9 \text{ cm}^3 \text{ mole}^{-1}$  [40]. Data for  $v_r$ -values are from an average of 8-12 swollen specimens, with reduced volume after drying i.e., corrected for sol volume fraction and elastically effective physical constraints. The variation of the



**Figure 1.** Variation of  $\mu_c$  with  $v_r$  for natural rubber (NR) crosslinked in the dry state. Crosslinking temperature = 120°C.

average  $v_r$  - values are within 95 % confidence limits, a range of  $\pm 2.2\%$  to  $\pm 5.5\%$  of the mean value. Variation of ( $\mu_c$ ) with ( $v_r$ ) is shown in Figure 1.

### Determination of Various Network Parameters

For natural rubber networks in toluene, Bristow and Watson reported  $\chi = 0.391$  from the equilibrium swelling measurements at 25°C from a single medium  $v_r$ -value of 0.2 [41]. The other reported value is 0.350 derived from heat of mixing measurements using gas liquid chromatography [42]. Difficulties in obtaining an applicable  $\chi$ -value for *cis* 1,4-polyisoprene in toluene warranted here the selection by trial within the range  $0.35 \leq \chi \leq 0.41$ , relying on the accuracy of the  $\mu_c$ -values.

TABLE 2. Network Parameters Based on the Equilibrium Swelling Measurements for Natural Rubber (NR) Crosslinked in the Dry State

Polymer Volume fraction** ( $v_f$ )	$\mu_E$ (mM.I <sup>-1</sup> )***				
	$\chi = 0.36$	$\chi = 0.37$	$\chi = 0.38$	$\chi = 0.39$	$\chi = 0.40$
0.0258	-	-	-	-	-
0.0359	-	-	-	-	-
0.0514	-	-	-	-	-
0.0671	16.7	16.7	16.9	17.4	18.5
0.0796	18.1	17.6	17.2	16.9	16.7
0.0983	22.7	21.8	20.9	20.1	19.3
0.1101	26.5	25.4	24.3	23.2	22.1
0.1151	28.3	27.0	25.8	24.7	23.5
0.1233	31.4	30.0	28.7	27.4	25.1

\* determined using the equation of state with  $v^{1/3}$  term.

\*\* corrected for sol fraction and physical constraint contribution.

\*\*\* after loose chain end correction.

Note that for a simple network of crosslink-junction functionality ( $\Phi = 4$ ), the introduced crosslink-junction density ( $\mu$ ) connecting  $N$  elastically effective segments is  $2N/\Phi$ . Experimental crosslink-junction densities were corrected for loose chain ends. All three equations of state were tested in the calculation of  $\mu_E$ -,  $N_E$ -, and  $M_E$ -values from swelling (see Table 2 for the  $\mu_E$ - values).

## RESULTS AND DISCUSSION

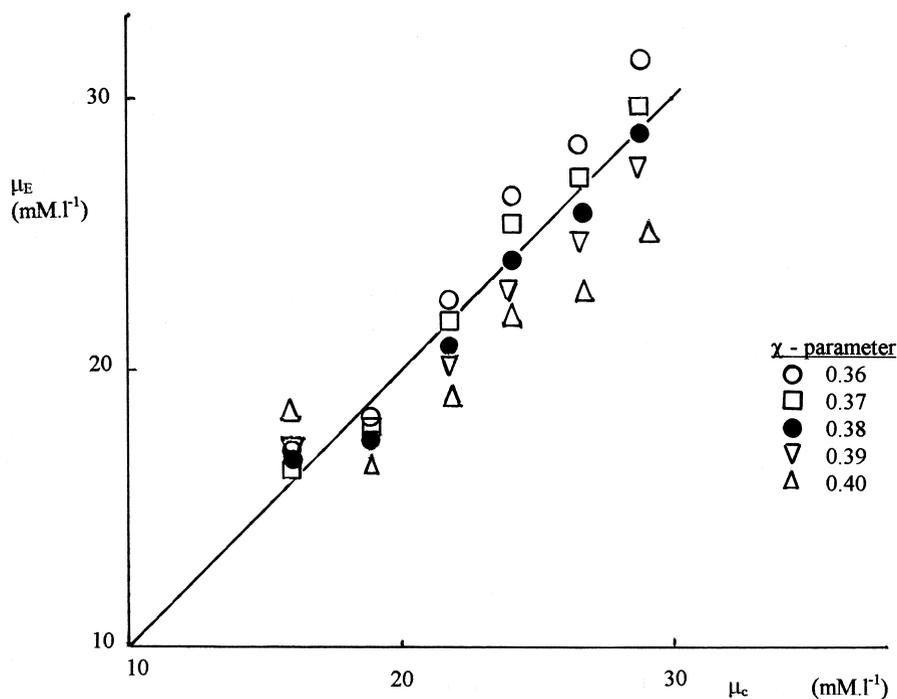
A large number of reported work on well characterized networks of polydienes [25, 33, 36, 43-46], and other rubbers with diene component [33] have relied on the relative simplicity of dicumyl peroxide as a precursor for effective and predictable reactions leading to crosslinks: DCP provides  $\Phi = 4$  networks with mole to mole correspondence of  $\mu_c$  and decomposed DCP [37-39].

As shown in Table 1, the crosslink-junction densities that have been designed fall within the low range  $9.1 \text{ mM.l}^{-1} \leq \mu_c \leq 29.2 \text{ mM.l}^{-1}$ , corresponding to  $5 \times 10^4 \text{ g mole}^{-1} \geq M_c \geq 1.6 \times 10^4 \text{ g mole}^{-1}$ .

Figure 1 shows the variation of  $\mu_c$  with  $v_r$ . The y-axis intercept measures a  $v_r$ , independent pre-swelling constraint present in the network ( $\epsilon = 2.3 \text{ mM.l}^{-1}$ ). This amount is presumed to account for the existing elastically effective physical constraints. The linearity of  $\mu_c$  vs.  $v_r$  plot enables the proportional corrections to the  $v_r$  values.

Similar to that of entanglement modulus for polymers in the melt-state [47], it is conceivable that beyond a critical  $\mu_c$  (here  $24 \text{ mM.l}^{-1}$ ), topological constraints such as entanglements that are held trapped between chemical crosslink-junctions assume greater contribution to network elasticity upon swelling. Numerous treatments deal with the quantitative valuation of permanent topologies as physical constraints resisting network swelling, in addition to chemically formed crosslink-junctions [48-58].

The corresponding  $\mu_E$ - values obtained from swelling measurements using the equation of state with the  $v_r^{1/3}$  term (Equation 1) and  $0.36 \leq \chi \leq 0.40$  are shown in Figure 2. It is found that agreement between  $\mu_c$  and a corresponding  $\mu_E$  occurs for  $\chi = 0.37$  at  $T = 25^\circ\text{C}$ . Similar attempts to verify the applicability of the modified equation of state (Equation 2) or the phantom model (Eqn. 4) for these networks showed their diversion. The modified equation of state is designed to fit networks with  $\Phi > 4$  but has been used by van der Hoff for polydiene networks crosslinked with DCP at high crosslink-junction density range of  $100 \text{ mM.l}^{-1} \leq v_r$

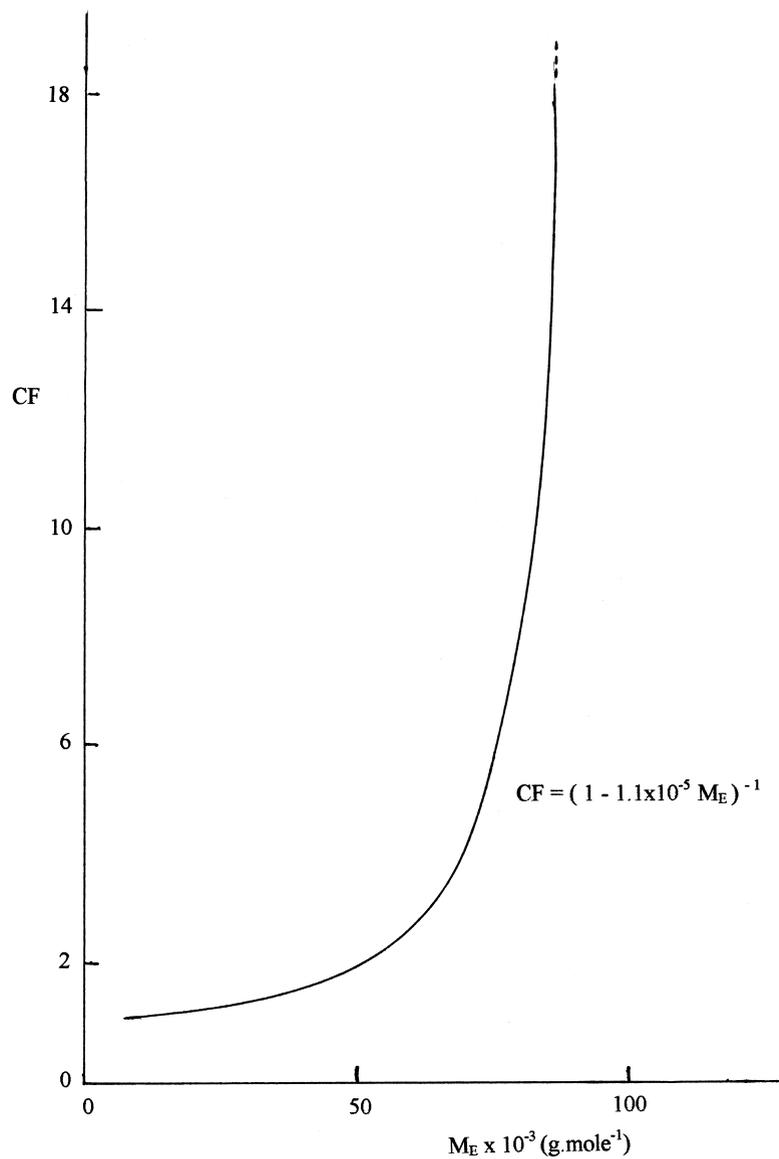


**Figure 2.** Correlation of crosslink-junction densities obtained from equilibrium swelling ( $\mu_E$ ) with values calculated from DCP decomposition kinetics ( $\mu_c$ ) for Natural rubber (NR) crosslinked in the dry state.

$\leq 175 \text{ mM.l}^{-1}$  [25] as well as other contributors [33] for EPDM networks at high crosslink-junction densities, up to  $1300 \text{ mM.l}^{-1}$ .

Figure 3 shows the correction function for loose chain ends for the prepared networks. It is evident that an average molecular weight between two chemically crosslinked-junctions remains valid (therefore, a network), for  $M_E < 1.1 \times 10^5 \text{ g mole}^{-1}$ . Otherwise, one is within the realm of the gelstate, with the state of a three-dimensional non-linear chain extensions rather than formed network.

At the very low chemical crosslink-junction densities found here, even though the swollen networks keep their dimensional integrity, they are not considered as formed networks below a predicted value  $\mu_c = 4.2 \text{ mM.l}^{-1}$ . The corresponding value obtained from swelling measurements with ( $\chi = 0.37$ ) is  $\mu_E = 4.6 \text{ mM.l}^{-1}$ .



**Figure 3.** Variation of the correction factor for the loose chain ends with  $M_E$ .  $M_n = 2.2 \times 10^5$  ( $\text{g mole}^{-1}$ ).

### CONCLUSION

The range of the experimentation presented here is within that for which the original Frenkel-Flory-Rehner equation is found to describe well the equilibrium state for swelling networks of natural rubber (*cis* 1,4-polyisoprene). The

appropriate network, solvent interaction parameter  $\chi = 0.37$  for natural rubber in toluene found here compares well, and is in tandem with the reported literature values of  $\chi = 0.391$  and  $\chi = 0.35$  obtained from the swelling and heat of mixing measurements, respectively.

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### REFERENCES

- [1] P. J. Flory, "*Principles of Polymer Chemistry*", Cornell University Press, Ithaca, NY, 1953, p. 464.
- [2] L. R. G. Treloar, "*The Physics of Rubber Elasticity*", 3rd Ed., Clarendon Press, Oxford, 1975, p. 60.
- [3] P. J. Flory, "*Principles of Polymer Chemistry*", Cornell University Press, Ithaca, NY, 1953, p. 497.
- [4] P. J. Flory, *J. Chem. Phys.*, *9*, 660 (1941).
- [5] P. J. Flory, *J. Chem. Phys.*, *10*, 51 (1942).
- [6] M. L. Huggins, *J. Chem. Phys.*, *9*, 440 (1941).
- [7] M. L. Huggins, *J. Chem. Phys.*, *46*, 151 (1942).
- [8] M. L. Huggins, *JACS*, *64*, 1712 (1942).
- [9] B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, *64*, 2035 (1958).
- [10] See for example P. C. Hiemenz, "*Polymer Chemistry*", Marcel Dekker, New York, 1984.
- [11] L. Y. Yen and B. E. Eichinger, *J. Poly. Sci. Poly. Phys. Ed.*, *16*, 117 (1978).
- [12] P. J. Flory, "*Principles of Polymer Chemistry*", Cornell University Press, Ithaca, NY, 1953, p. 515.
- [13] J. Frenkel, *Acta. Phisicochim.*, USSR, *9*, 1938, p. 235.
- [14] J. Frenkel, *Rubber Chem. Tech.*, *13*, 264 (1940).
- [15] P. J. Flory and J. Rehner, *J. Chem. Phys.*, *11*, 512 (1943).
- [16] P. J. Flory and J. Rehner, *J. Chem. Phys.*, *11*, 521 (1943).
- [17] P. J. Flory, *J. Chem. Phys.*, *12*, 412 (1944).

- [18] P. J. Flory, *J. Chem. Phys.*, *18*, 108 (1950).
- [19] J. J. Hermans, *Trans. Faraday Soc.*, *43*, 591 (1947).
- [20] M. J. Voorn and J. J. Hermans, *J. Poly. Sci.*, *35*, 113 (1959).
- [21] P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, NY, 1953, p. 577.
- [22] H. James and E. Guth, *J. Chem. Phys.*, *15*, 669 (1947).
- [23] P. J. Flory, *J. Am. Chem. Soc.*, *63*, 3083 (1941).
- [24] P. J. Flory and B. Erman, *Macromolecules*, *15*, 800 (1982).
- [25] B. M. E. van der Hoff, *Ind. Eng. Chem. Prod. Res. Dev.*, *2(4)*, 273 (1963).
- [26] R. S. Jessup, *J. Res. Natl. Bur. Stds.*, *60*, 47 (1958).
- [27] G. Gee, *J. Chem. Phys.*, 280 (1947).
- [28] W. G. Lloyd and T. Alfrey, Jr., *J. Poly. Sci.*, *62*, 159 (1962).
- [29] G. B. Mc Kenna, K. M. Flynn, and V. Chen, *Poly. Commun.*, *29*, 272 (1988).
- [30] G. B. Mc Kenna, *Macromolecules*, *22*, 4507 (1989).
- [31] G. B. Mc Kenna, *Polymer*, *31*, 1937 (1990).
- [32] S. P. Malone, C. Vosburgh, and C. Cohen, *Polymer*, *34 (24)*, 5149 (1993).
- [33] Z. Hrnjak-Murgic, J. Jelencic, M. Bravar, and M. Marovic, *J. Appl. Poly. Sci.*, *65*, 991 (1997).
- [34] J. J. Hermans, *J. Poly. Sci.*, *59*, 191 (1962)
- [35] P. J. Flory, *J. Am. Chem. Soc.*, *63*, 3083 (1941).
- [36] D. K. Thomas, *J. Appl. Poly. Sci.*, *6*, 613 (1962).
- [37] L. A. Wood, *J. Res. Natl. Bur. Stds.*, *A 80*, 451 (1977).
- [38] L. A. Wood, *Rubber Chem. Tech.*, *50*, 233 (1977).
- [39] L. A. Wood, *J. Res. Natl. Bur. Stds.*, *76 A(1)*, 51 (1972).
- [40] G. M. Bristow and W. F. Watson, *Trans. Faraday Soc.*, *54*, 1731 (1958).
- [41] G. M. Bristow and W. F. Watson, *Trans. Faraday Soc.*, *54*, 1567 (1958).
- [42] Y. B. Tewari and H. P. Schreiber, *Macromolecules*, *5(3)*, 329 (1972).
- [43] see Ref. 25 for a comprehensive list of articles dating prior to 1963.
- [44] G. M. Bristow, *J. Appl. Poly. Sci.*, *9*, 1571 (1965).
- [45] C. S. M. Ong and R. S. Stein, *J. Poly. Sci. Poly. Phys. Ed.*, *A-2*, 1599 (1974).
- [46] S. Kaang, D. Gong, and C. Nah, *J. Appl. Poly. Sci.*, *65*, 917 (1997).
- [47] See for example, P. G. de Gennes, "Scaling Concepts in Polymer Physics", Cornell University Press, Ithaca, New York, 1979, p. 221.
- [48] W. W. Graessley, *Adv. Poly. Sci.*, *47*, 67 (1982).
- [49] D. S. Pearson and W. W. Graessley, *Macromolecules*, *13*, 1001 (1980).

- [50] L. M. Dossin and W. W. Graessley, *Macromolecules*, *12*, 673 (1979).
- [51] W. W. Graessley, *Adv. Poly. Sci.*, *16*, 1 (1974).
- [52] N. R. Langley, *Macromolecules*, *1*, 348 (1968).
- [53] M. Gottlieb and R. J. Gaylord, *Macromolecules*, *17*, 2024 (1984).
- [54] M. Gottlieb and R. J. Gaylord, *Polymer*, *24*, 1644 (1983).
- [55] S. F. Edwards and T. A. Vilgis, *Polymer*, *27*, 483 (1986).
- [56] F. Horkay and M. Zrinyi, *Macromolecules*, *15*, 1306 (1982).
- [57] E. Geissler and A. M. Hecht, *Macromolecules*, *14*, 185 (1981).
- [58] J. Bastide, C. Picot, and S. Candau, *J. Macromol. Sci. Phys.*, *B-19*, 13 (1981).

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