

Rigid Polymer Networks

By S. M. Aharoni, S. F. Edwards

With 51 Figures



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Preface

Synthetic rigid polymer networks comprise part for the thermosetting class of polymers. Some members have now been in use for about a hundred years. These first pioneers, such as the phenol formaldehydes and furfurals, owed their popularity to a combination of several important features: monomer availability, ease and speed of processing, low cost of monomers, process and end-products, ability to be filled by various fillers, and a very desirable combination of good mechanical properties, high gloss surface, and excellent electrical insulation. As time progressed, the potential users elevated the performance requirements of the rigid polymer networks demanding ever-increasing thermal stability and mechanical properties. In response to these increasing expectations, novel rigid polymer networks were created with increasing fractions of thermally stable and mechanically robust moieties, initially as single rings and later as condensed aromatic groups. Laterly, rigid polymer networks whose stiff segments are liquid crystalline in nature were also introduced. In this case, very high modulus and strength may be obtained by first orienting the segments in the desired direction and then setting them in their final form by the addition or in-situ creation of rigid junctions.

As we delved into the subject matter, we were struck by the huge amount of literature dealing with various synthetic aspects of rigid polymer networks, the smaller number of publications dealing with correlations between the molecular structure of the networks and commercially desirable properties, and the far smaller number of publications, devoted to fundamental theoretical description of these networks, their properties, evolution and final structure, and the unique synthetic limitations imposed by the inherent rigidity of the structural units of the growing networks. The remarkably broad range of rigid polymer networks and the great ingenuity invested in their creation stood in stark contrast to the dearth of theoretical interest. It may be that the factor which made them theoretically less than popular is that so much of the literature in the field is patent literature, and the non-Gaussian, non-elastomeric nature of the rigid polymer networks, both alien to most theoreticians.

In this work we aim, therefore, to present the reader with an up-to-date overview of the field of rigid polymer networks with many of its synthetic complexities and challenges, and to whet the appetite of theoreticians and encourage them to solve the many fascinating theoretical problems presently existing in the field.

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Table of Contents

List of Symbols	xiii
1 Introduction	1
1.1 Definitions.	1
1.2 General Classification of Liquid-Crystal Polymers and Networks.	7
1.2.1 Definition of Liquid-Crystal Polymers.	8
1.2.2 Flexible Chain Polymers with Mesogenic Groups	10
1.2.3 Networks with Flexible Chains and Stiff Mesogenic Groups	13
1.2.3.1 Networks with Stiff Main-Chain Mesogens, Flexible Spacers and Flexible Junctions.	13
1.2.3.2 Networks with Stiff Main-Chain Mesogens, Flexible spacers and Rigid Branchpoints	16
1.2.3.3 Networks with Stiff Pendant Mesogens, Flexible Main-Chains and Flexible Junctions	18
1.2.3.4 Networks with Stiff Pendant Mesogens Connected at Both Ends to Flexible Main Chains	21
1.2.4 Networks Containing No Flexible Spacers	25
1.2.4.1 Uniform Main-Chain Mesogenicity: Flexible, Wormlike, Rodlike	26
1.2.4.2 LCPs from Biological Origin and Their Networks.	33
1.2.4.3 Networks with Uniform Main-Chain Mesogenicity and Flexible Crosslinking Residues	34
1.3 The Fractal Character of Pre-Gel and Post-Gel Highly Branched Polymers.	38
2 Exclusions	43
3 Synthetic Highlights	46
3.1 One-Step and End-Capped Rigid Networks.	46
3.1.1 Networks with Stiff Hydrocarbon Segments	46
3.1.1.1 Polyphenylenes and Poly (Substituted Phenylenes)	46
3.1.1.2 Hydrocarbon Networks with Very Short Aromatic Segments.	48

3.1.1.3	Stiff Aliphatic Segments	52
3.1.1.4	Overview.	52
3.1.2	Aromatic Polyamide Networks with Stiff Segments and Rigid Branchpoints	54
3.1.2.1	Rigid Polyamide Networks, Gels and Fractal Polymers Prepared in Solution in the Presence of Triarylphosphite.	54
3.1.2.2	Rigid Polyamide Networks and Fractal Polymers Prepared in Solution by Other Procedures.	66
3.1.3	Rigid Aromatic Polyester Networks	68
3.1.4	Rigid Aromatic Networks Containing Single-Atom Bridges . 70	
3.1.4.1	Aromatic Hydrocarbons with Methylene Bridges	72
3.1.4.2	Phenol-Formaldehyde Type Networks	73
3.1.4.3	Furan-Containing Networks	76
3.1.4.4	Aromatic Polyether and Ether-Containing Networks	78
3.1.4.5	Bridged Aromatic Networks with Uncommon Electronic Structure	80
3.1.4.6	Morphology and Possible Fractality	84
3.1.5	Rigid Networks with Triazine Branchpoints	85
3.1.6	Rigid Networks from Stiff End-Capped Segments	92
3.1.6.1	Networks with Unsaturated Imide Junction Precursors	93
3.1.6.2	Networks Crosslinked by Strained-Ring Precursors . 96	
3.1.6.3	Networks Crosslinked by Ethynyl End-Caps and Pendant Groups.	102
3.2	Two-Step Aromatic Networks	107
3.2.1	Two-Step Aromatic Polyamide Networks.	108
3.2.2	Two-Step Networks from Poly (Ether Ketone Ketone) (PEKK).	112
3.2.3	Networks from Aromatic Linear Chains Created by Reacting Backbone Diacetylene or Pendant Acetylene Groups	113
3.2.4	Potential Two-Step Polyarylene Networks	116
3.2.5	Supernetworks.	117
4	Features	121
4.1	Pre-Gel State	121
4.1.1	Fractal Nature of Growing One-Step Species and Comparison with Two-Step Species.	121
4.1.2	C_0^* , the Critical Concentration for Gelation	135
4.2	Post-Gel State	142
4.2.1	Fractal Nature of Gelled Rigid Networks.	142
4.2.2	Manifestations of Rigid Network Defects	149
4.2.3	Mechanical Properties of Rigid Networks and Their Gels . 152	

4.2.4	Observations on Effects of Gravity and Flow-Stress During the Formation of Rigid Network Gels	155
4.2.5	High Temperature Stability of Rigid Aromatic Networks	157
4.3	Some Properties of Liquid-Crystal Polymer Networks	159
4.4	Modes of Segmental Deformation	161
4.4.1	Description of Segments	161
4.4.1.1	Mathematical Description of the Molecules	161
4.4.1.2	General Empirical Description of Network Segments	164
4.4.2	Deformation of Aromatic Segments with Bridges Consisting Exclusively of Coaxial Single Bonds	166
4.4.3	Deformation of Stiff Aromatic Segments with Bridges Consisting of a Single Non-Coaxial Bond Connecting Two Coaxial Bonds Between Aromatic Groups	168
4.4.4	Deformation of Aromatic Segments with Swivels Consisting of Two Single Bonds Connected by a Single Atom	175
4.4.5	Deformation of Networks with Stiff Aromatic Segments and Relatively Flexible Aliphatic Junctions Created from Reactive End-Caps	177
4.5	Questions of Elastic Constants	179
5.	Theory	192
5.1.	The Problem	193
5.1.1	Responses of Flexible and Rigid Networks to Stress Fields	193
5.1.2	Complexities Uniquely Linked to Network Rigidity	193
5.2	Theoretical Description of Rigid Networks	194
5.2.1	One-Step Networks	194
5.2.1.1	General Mathematical Description	200
5.2.1.2	Field Formalism for Deformation	203
5.3	Simpler Theoretical Approaches	206
5.3.1	Simple Calculations of the Concentrated Rigid Network	206
5.3.2	Simple Calculations in a Dilute Rigid Network	208
6	References	214
	Author Index Volumes 101–118	233
	Subject Index	239

List of Symbols, Abbreviations and Acronyms

a	Persistence length
a	Average tube diameter, network mesh size
a	Coefficient in replica procedure in Sect. 5
A	Kuhn segment length
A	Free energy of a particular member of an ensemble
\tilde{A}	Free energy of the deformed state
$\langle \tilde{A} \rangle$	Average free energy of the deformed state
A_{el}	Elastic free energy
Ar	Aromatic unit in chain or pendant group
c	Concentration
C	Equilibrium concentration of gel
C_0	Polymer concentration in "as prepared" gel
C_0^*	Critical concentration for "infinite" network formation
C_f	Number density of fractal polymers
C_n	Characteristic ratio of chain with n bonds
C_∞	Characteristic ratio of a chain in the limit of infinity
$\cos \theta$	Angular energy
d	Average diameter of chain or segment
d^2	Effective segment cross-sectional area
D	Bond dissociation energy
D	Fractal dimension
D_s	Fractal surface dimensionality
D_f	Fractal mass dimensionality
\overline{DP}	Degree of polymerization
DP	Average degree of polymerization of chain or segment
DABA	4,4'-Diaminobenzanilide
DLA	Diffusion limited aggregation
DMAc	N,N-Dimethylacetamide
DMF	N,N-Dimethylformamide
e_{ij}	Strain
E	Strain modulus
E	Young's modulus of reinforced ensemble
E_f	Young's modulus of reinforcing fiber or segment
E_l	Longitudinal tensile modulus
E_n	Young's modulus of the bulk or matrix
E_r	Rod material modulus
f	Branchpoint or junction functionality
f	Tensile force applied to segment
\bar{f}	Average retractive force
F	Force
FP, FPs	Fractal polymer, fractal polymers
$g(r_1 r_2)$	Mathematical description of monomer in Sect. 5

G	Equilibrium shear modulus
H-bond	Hydrogen bond
ΔH_a	Activation energy for glass transition
$\langle h^2 \rangle_0$	Average square unperturbed end-to-end distance
I(q)	Intensity of scattered radiation at q
IR	Infrared
k	Boltzman constant
K_i	Force constants
l	Length of actual or virtual bond; average bond length
l_0	Length of average stiff or flexible segment in network or FP
L	Chain contour length
L	Total length of segments in a FP
L_c	Segment length between entanglements
LALS	Low angle light scattering
M	Molecular weight
M_c	Molecular weight between entanglements
M_n	Number average molecular weight
M_w	Weight average molecular weight
N	Number of repeat units
N	Number density of rods, rodlike segments
N_F	Number of FPs
NF	Network fragment
NMP	<i>N</i> -Methyl-2-pyrrolidinone
NMR	Nuclear magnetic resonance
NTPA	Nitroterephthalic acid
P	Fraction of monomer consumed, probability that monomer was consumed
P	Probability
Py	Pyridine
PPh_3	Triphenylphosphine
q	Scattering vector
r	Displacement length of a chain or segment
r	Chain or segment end-to-end vector
$\langle r^2 \rangle_0$	Mean square magnitude of r
R	Aliphatic or general organic unit in chain, segment or pendant group
R	Gas constant
R	Radius of polymeric species, radius of FP
R_a	Average distance between centers of FPs
R_G	Radius of gyration
R_H	Hydrodynamic radius
R_{GW}	Radius of gyration of worm-like chain
R_1	Length of non-coaxial, actual bond in polyamide segment
R_2	Length of coaxial, virtual bond in polyamide segment

s	Area
S	Entropy
S	Spring constant
SANS	Small angle neutron scattering
SAXS	Small angle X-ray scattering
T	Absolute temperature
T_g	Glass transition temperature
$T_{g\infty}$	Glass transition temperature of uncrosslinked polymer
TPA	Terephthalic acid
TPP	Triphenylphosphite
U_0	Thermal activation energy for bond scission
v	Volume
V	Potential energy of rod
$V(l)$	Potential energy of bond
V_f	Volume fraction
WAXD	Wide-angle X-ray diffraction
x	Numerical value of DP
x	Axial ratio
\bar{X}	Axial ratio of stiff segment of average length
\bar{X}^*	Critical axial ratio for the onset of liquid crystallinity
Z_f	Number of reactive groups belonging to all species larger than monomers
Z_m	Number of reactive groups belonging to monomers
α	Valence angle of carbonyl in amide group
α_G, α_L	Coefficients of expansion in the glass, liquid states
β	Valence angle at nitrogen in amide group
γ	Stress concentration factor for brittle failure
ε	Strain
θ	Scattering angle, angle between segment axis of symmetry and network draw direction
λ	Wavelength of scattered beam
λ	Measure of tube deformation, extension
λ	Measure of material deformation
Λ	Deformation matrix
μ	Shear modulus
ν	Number concentration of elastically effective network segments
ρ	Polymer density
σ	Stress
σ_b	Breaking strength
ϕ	Torsional angle around bond between aromatic ring and nitrogen in amide group
ϕ	Volume concentration
ϕ, ϕ^*	Parameters used in integrations in Sect. 5
Φ	1% Extensibility

Ψ	Torsional angle around bond between aromatic ring and carbon in amide group
ω	Torsional angle around central bond in amide group
ω	Stress concentration factor for ductile failure
$\iint \phi g \phi$	Mathematical representation of unreacted monomer in Sect. 5
$\iint \phi^{*2}$	Mathematical representation of difunctional monomer in Sect. 5
$\int \phi^{*3}$	Mathematical representation of trifunctional monomer in Sect. 5