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Isomeric Graft Copolymers and Interpenetrating Polymer Networks. Possible Arrangements and Nomenclature

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ABSTRACT: A nomenclature scheme is proposed for graft copolymers and interpenetrating polymer networks. Tables of reactive unit combinations and sets of operations are presented together with examples of possible reaction sequences. The new nomenclature scheme is based on group theory concepts.

At the present time, the scientific and patent literature describes over 150 distinguishable ways of organizing two kinds of polymer molecules in space.[1,2] While such materials encompass the polymer blends, grafts, blocks, and interpenetrating polymer networks (IPN's), the largest number of compositions actually synthesized are classified as graft copolymers. With the present nomenclature, a graft copolymer can be written poly(A-g-B), where the A and B represent the two initial monomers,[3,4] and the first mentioned symbol represents the backbone chain while the second represents the side chain. The symbol g stands for "graft".

However, the order of the synthetic steps, the presence or absence of cross-linking, and the actual mode of grafting have received inadequate attention in part because of an inadequate nomenclature. Besides the intrinsic value of accurate detail per se, the morphology of the materials so formed and hence their physical and mechanical properties are strongly influenced by the synthetic sequence. The present paper has the dual purpose of describing a proposed graft copolymer nomenclature, and presenting the results of a computer-based study on the use of this nomenclature to generate some of the possible, but not yet synthesized, combinations. Although the scheme to be outlined below remains woefully incomplete, some tens of thousands of distinct possibilites are shown possible. For general reader use, a small sampling of the more interesting synthetic possibilities is included below. The description of the computer program is shown in Appendix I. (The computer program proper is available through the courtesy of the authors.) The development of the pertinent nomenclature involves the use of group theory concepts, which have been recently applied to polymer blends, grafts, and blocks. The present report employs a simplified version of the above-mentioned theory.

In presenting a proposed nomenclature scheme, it is appropriate to mention a few of the many papers to which it would apply. Recent symposia have been edited by Ceresa,[5] Burke and Weiss,[6] Aggarwal,[7] Molau,[8] Gould,[9] Platzer,[10] and Sperling.[11] Works by Rogers,[12] Frisch,[13–15] Ryan,[16] Amagi, Ohya, Shuki, and Yusa,[17] Johnson and Labana,[18] Vollmert,[19] and Sperling[20,21] bear on the problem. Klempner and Frisch[13] have also provided an independent nomenclature scheme.

The present group theory development remains incomplete, however, special symbols being required in writing nomenclature for the AB cross-linked copolymers of Bamford, Eastmond, and Whittle,[22] and the star-block copolymers of Bi and Fetters.[23]

Basic Nomenclature

As basic elements, we will consider momomer 1, monomer 2, . . . , monomer n, which can be polymerized to form various polymers and copolymers. As the basic reactive units, we designate the following in Chart I. The operations employed are designated in Chart II. Polymerization will be assumed to be linear unless the operation C is specified. Most importantly, the present group is noncommutative, and the time sequence of events must be preserved. Thus, the order of the operations must be maintained. One of the key findings to be explored below is that we must increase our sensitivity to the order of the operations in more complex cases, and not assume, for example, that cross-linking followed by grafting is identical with grafting followed by cross-linking.

The operations and the reactive units must be clearly distinguished. To differentiate between operations and the objects upon which the group operates (the reactive units), capital and lower case letters will be employed, respectively. For example, the addition of monomer will be designated as m. The addition of monomers capable of inducing grafting or cross-linking, e.g., divinylbenzene, will be designated by g and c, respectively. The operations of grafting and cross-linking, which may come much later in the reaction sequence, will be specified by the capital letters.

We must also consider a series of inverse operations.[1,2]

Chart I

Reactive unit	Interpretation
m_1	monomer 1
m_2	monomer 2
c_1	cross-linker 1
c_2	cross-linker 2
g_1	grafting agent for 1
g_2	grafting agent for 2

Chart II

Operation	Interpretation
P_1	polymerization of monomer 1
P_2	polymerization of monomer 2
C_1	cross-linking of 1
C_2	cross-linking of 2
G_{12}	grafting of 2 to 1
G_{21}	grafting of 1 to 2

Table I
Reactive Unit Combinations (with m_1 and m_2)

1\. m_1
2\. m_1c_1
3\. m_1g_1
4\. m_1m_2
5\. m_1c_2
6\. m_1g_2
7\. $m_1c_1g_1$
8\. $m_1c_1m_2$
9\. $m_1c_1c_2$
10\. $m_1c_1g_2$
11\. $m_1g_1m_2$
12\. $m_1g_1c_2$
13\. $m_1g_1g_2$
14\. $m_1m_2c_2$
15\. $m_1m_2g_2$
16\. $m_1c_2g_2$
17\. $m_1c_1g_1m_2$
18\. $m_1c_1g_1c_2$
19\. $m_1c_1g_1g_2$
20\. $m_1c_1m_2c_2$
21\. $m_1c_1m_2g_2$
22\. $m_1c_1c_2g_2$
23\. $m_1g_1m_2c_2$
24\. $m_1g_1m_2g_2$
25\. $m_1g_1c_2g_2$
26\. $m_1m_2c_2g_2$
27\. $m_1c_1g_1m_2c_2$
28\. $m_1c_1g_1m_2g_2$
29\. $m_1c_1m_2c_2g_2$
30\. $m_1g_1m_2c_2g_2$
31\. $m_1c_1g_1c_2g_2$
32\. $m_1c_1g_1m_2c_2g_2$
33\. m_2
34\. m_2c_1
35\. m_2g_1
36\. m_2c_2
37\. m_2g_2
38\. $m_2c_1g_1$
39\. $m_2c_1c_2$
40\. $m_2c_1g_2$
41\. $m_2c_2g_2$
42\. $m_2g_1c_2$
43\. $m_2g_1g_2$
44\. $m_2c_1g_1c_2$
45\. $m_2c_1c_2g_2$
46\. $m_2c_1g_1g_2$
47\. $m_2g_1c_2g_2$
48\. $m_2c_1g_1c_2g_2$

Thus, P^{-1} is introduced as depolymerization, G^{-1} as degrafting, C^{-1} as decross-linking. In this context, C and C^{-1} are inverse. Thus, $CC^{-1} = I$, where I represents the mathematical identity. In more chemical terms, the reaction was reversed.

As discussed elsewhere,[1,2] simultaneous operations can be placed in parentheses. Thus, parentheses will be used to distinguish operations which happen at the same time from those that occur sequentially in time. Square brackets will be employed to distinguish separate polymerizations, of which their products are later mixed and/or reacted. In a formal sense, the parentheses and brackets constitute operations in their own right. For simplicity, neither inverse operations nor brackets will be considered in the computer study.

The polymer molecule will be associated with the designated operation with the use of the subscripts 1, 2, etc. Thus, P_1 indicates polymerization of m_1. The operation G will be specified by both subscripts, the order of the subscripts indicating respectively the backbone and the branch side chain. (Identical subscripts could, of course, be used to indicate homopolymer branching.)

A few examples are in order. The combination

$$[m_1P_1][m_2P_2] \tag{1}$$

represents a mixture of two linear polymers, as in a simple mechanical blend. A simple graft copolymer may be written

$$m_1P_1m_2(P_2G_{12}) \tag{2}$$

The combination

$$m_1(P_1C_1)m_2(P_2G_{12}) \tag{3}$$

refers to a simple semi-IPN of the first kind. A semi-IPN is a graft copolymer where one, but not both, constituent is cross-linked. Note that the order of the operations is important. For example,

$$m_1P_1m_2(P_2G_{12})C_1 \neq m_1(P_1C_1)m_2(P_2G_{12}) \tag{4}$$

the left-hand side indicating a post-cross-linking operation for polymer 1, and the right-hand side indicating that the cross-links in polymer 1 are introduced during polymerization.

Reactive Units and Operations Sequences

In the following, several approximations have been made for simplicity.

Table II
Sets of Operations

101\. P_1
102\. P_2
103\. C_1
104\. C_2
105\. G_{12}
106\. G_{21}
107\. P_1P_2
108\. P_1C_1
109\. P_1C_2
110\. P_1G_{12}
111\. P_1G_{21}
112\. P_2C_1
113\. P_2C_2
114\. P_2G_{12}
115\. P_2G_{21}
116\. C_1C_2
117\. C_1G_{12}
118\. C_1G_{21}
119\. C_2G_{12}
120\. C_2G_{21}
121\. $G_{12}G_{21}$
122\. $P_1P_2C_1$
123\. $P_1P_2C_2$
124\. $P_1P_2G_{12}$
125\. $P_1P_2G_{21}$
126\. $P_1C_1C_2$
127\. $P_1C_1G_{12}$
128\. $P_1C_1G_{21}$
129\. $P_1C_2G_{12}$
130\. $P_1C_2G_{21}$
131\. $P_1G_{12}G_{21}$
132\. $P_2C_1C_2$
133\. $P_2C_1G_{12}$
134\. $P_2C_1G_{21}$
135\. $P_2C_2G_{12}$
136\. $P_2C_2G_{21}$
137\. $P_2G_{12}G_{21}$
138\. $C_1C_2G_{12}$
139\. $C_1C_2G_{21}$
140\. $C_1G_{12}G_{21}$
141\. $C_2G_{12}G_{21}$
142\. $P_1P_2C_1C_2$
143\. $P_1P_2C_1G_{12}$
144\. $P_1P_2C_1G_{21}$
145\. $P_1P_2C_2G_{12}$
146\. $P_1P_2C_2G_{21}$
147\. $P_1P_2G_{12}G_{21}$
148\. $P_1C_1C_2G_{12}$
149\. $P_1C_1C_2G_{21}$
150\. $P_1C_1G_{12}G_{21}$
151\. $P_1C_2G_{12}G_{21}$
152\. $P_2C_1C_2G_{12}$
153\. $P_2C_1C_2G_{21}$
154\. $P_2C_1G_{12}G_{21}$
155\. $P_2C_2G_{12}G_{21}$
156\. $C_1C_2G_{12}G_{21}$
157\. $P_1P_2C_1C_2G_{12}$
158\. $P_1P_2C_1C_2G_{21}$
159\. $P_1P_2C_1G_{12}G_{21}$
160\. $P_1P_2C_2G_{12}G_{21}$
161\. $P_1C_1C_2G_{12}G_{21}$
162\. $P_2C_1C_2G_{12}G_{21}$
163\. $P_1P_2C_1C_2G_{12}G_{21}$

(1) Only two types of monomer, cross-linker, and grafting agent are permitted, designated by subscript 1's and 2's.

(2) Each reactive unit can be added only once, and each operation can be carried out only once.

(3) Random copolymerization between the 1's and 2's is prohibited. (Different polymerization modes, such as addition and condensation, must be assumed when m_1 and m_2 appear together.)

(4) No inverse reactions are assumed.

(5) No blending operations requiring brackets are assumed.

(6) Grafting and cross-linking reactive groups are always explicitly written. In practice, grafting and cross-linking may or may not require specific reactive units. In addition, the operations of grafting or cross-linking may occur before, during, or after polymerization.[24,25] Grafting or cross-linking before polymerization has the meaning of forming the pertinent site first, to be followed by polymerization. For example, the reaction

Table III
Addition of Monomer 1 and Other Reactive Units after Monomer 2 has Already Been Added

m_1	m_1g_2	$m_1c_2g_1$	$m_1c_1c_2g_2$
m_1c_1	$m_1c_1c_2$	$m_1c_2g_2$	$m_1c_1g_1g_2$
m_1c_2	$m_1c_1g_1$	$m_1g_1g_2$	$m_1c_2g_1g_2$
m_1g_1	$m_1c_1g_2$	$m_1c_1c_2g_1$	$m_1c_1c_2g_1g_2$

Table IV
Addition of Monomer 2 and Other Reactive Units after Monomer 1 has Already Been Added

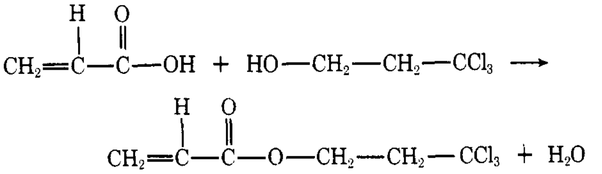
m_2	m_2g_2	$m_2c_2g_1$	$m_2c_1c_2g_2$
m_2c_1	$m_2c_1c_2$	$m_2c_2g_2$	$m_2c_1g_1g_2$
m_2c_2	$m_2c_1g_1$	$m_2g_1g_2$	$m_2c_2g_1g_2$
m_2g_1	$m_2c_1g_2$	$m_2c_1c_2g_1$	$m_2c_1c_2g_1g_2$

Table V
Reactive Unit Combinations Excluding Monomers

49. c_1
50. c_2
51. g_1
52. g_2
53. c_1c_2
54. c_1g_1
55. c_1g_2
56. c_2g_1
57. c_2g_2
58. g_1g_2
59. $c_1c_2g_1$
60. $c_1c_2g_2$
61. $c_1g_1g_2$
62. $c_2g_1g_2$
63. $c_1c_2g_1g_2$

Table VI
A Short List of Possible Reaction Sequences

1. $m_1P_1c_1C_1m_2P_2c_2C_2g_1G_{12}g_2G_{21}$
2. $m_1P_1c_1C_1(m_2c_2g_1g_2)(P_2C_2G_{12})$
3. $(m_1c_1m_2)P_1c_2C_2g_1G_{12}C_1$
4. $(m_1c_1m_2)(P_1C_1)(c_2g_2)G_{21}g_1(P_2G_{12})$
5. $m_1P_1c_1C_1(m_2g_2)(P_2G_{21})g_1G_{12}c_2C_2$
6. $(m_1c_2g_2)P_1(m_2c_1g_1)(P_2C_1G_{12})$
7. $(m_1c_1m_2c_2)(P_1P_2C_1C_2)g_1G_{12}g_2G_{21}$



$$\mathrm{CH_2{=}\overset{H}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-OH + HO-CH_2-CH_2-CCl_3 \longrightarrow CH_2{=}\overset{H}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CCl_3 + H_2O} \tag{5}$$

forms a potential graft site, where the vinyl group can be polymerized, and the CCl_3 group can later serve to initiate a second polymerization.[1]

A set of symbols representing reactive units is written first, followed by a possible set of operations. A set of reactive units disjoint with the first is then introduced, followed by a second set of possible operations disjoint with the first set. The process is repeated until all possible reactions have been carried out. The sequence, if interrupted at any point, also yields a viable, realistic material (but then, not necessarily a graft copolymer!). Such a material may or may not contain little molecules, however, depending on the sequence and point of interruption.

The sets of reactive units to be initially chosen are shown in Table I. The collection of the sets of operations to be added next is shown in Table II. (The computer program, as in real life, was written so that only possible sets of operations followed the reactive units. For example, P_1 could not appear unless m_1 had been previously introduced.) As shown in Appendix I, Tables III, IV, and V may be employed for subsequent selection of reactive units.

Table VI samples the results of the computer program. Since many thousands of possibilities exist, even for this simplified treatment, no attempt at completeness was made in constructing Table VI. The reader is referred to ref 1 and 2 for many other examples.

It may be that future readers would wish to employ the numbering system that accompanies the reactive units and operations in Tables I–V. For example, the last sequence in Table VI could be written.

$$20\text{-}142\text{-}51\text{-}105\text{-}52\text{-}106 \tag{6}$$

Numbers below 100 refer to reactive units, and numbers between 101 and 199 refer to operations.

Nomenclature Adoption

Clearly the above scheme does not give chemical details, molecular weights, or even relative amounts of the various components added. However, the advantage of the suggested nomenclature lies in its concise topological description of complex reaction sequence. The scheme is, of course, clearly not limited to the combinations presented herein, but should also make use of the bracket terminology for blending combinations[1,2] and inverse reactions for controlled degradation. The proposed nomenclature was submitted to the Nomenclature Committee of the Polymer Division of the American Chemical Society for consideration, and the authors would appreciate any comments or suggestions from the audience of working scientists and engineers at large.

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Appendix I

Brief Program Description

(1) Pick reactive unit set from Table I.
(2) Pick a permissible operation unit set from Table II.
(3) Pick further permissible reactive unit set from Tables III–V.
(4) Pick further permissible operation set from Table II.
(5) Repeat steps 3 and 4 until each reactive unit and operation unit has been chosen once and only once. There are now N sets.
(6) Print this combination.
(7) Replace the N-th set with a new permissible set from the appropriate table.
(8) Print this new combination.
(9) Repeat steps 7 and 8 for all permissible combinations.
(10) Replace the $N - 1$ set with a new permissible set.
(11) Print this combination.
(12) Add a new permissible set to this combination.
(13) Print resulting combination.
(14) Replace this set with a different permissible set.
(15) Print resulting combination.
(16) Repeat steps 14 and 15 for all combinations.
(17) Repeat steps 12 to 16 for all combinations.
(18) Repeat steps 10 to 17 for all combinations.
(19) Let $N = N - 1$ and return to step 10.
(20) Repeat steps 10 to 19 until all permissible combinations have been formed.

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Anionic Polymerization of Butadiene in Tetrahydrofuran. I. Isomerization of Polybutadienyl Salts

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ABSTRACT: The near-uv absorption spectra of polybutadienyllithium, -sodium, and -potassium have been investigated at various temperatures in tetrahydrofuran. It was observed that these changed with temperature and also could depend on the presence or absence of a polymerization reaction. These changes are correlated with differing cis and trans populations of the active center. With the lithium and sodium compounds the cis content at equilibrium increases with decreasing temperature. The monomer addition step favors the formation of trans active centers, and at low temperatures the cis–trans population deviates markedly from equilibrium. Polybutadienylpotassium shows more complex behavior. An irreversible isomerization to another form of the active center masks the simple cis–trans isomerization.

Early studies of the electronic spectra of anionic polymerization systems particularly in polar solvents have shown that the growing active centers are not always stable. Besides attack on the solvent leading to a decrease in their concentration, so-called isomerization reactions can occur, often leading to new species which are inactive in further homopolymerization. Such is the case with polystyrylsodium in tetrahydrofuran[1,2] (THF), although this fortunately is a relatively slow reaction. Anions of the diene monomers are even less stable in this solvent at room temperature[3,4] although stability is better at lower temperatures.[5] Some of the dienyl anions, e.g., polyisoprenyllithium can re-form the original anions after isomerization by the addition of further monomer. Recent studies of oligomeric polyisoprenyl- and polybutadienyllithium have indicated that both cis and trans forms of the active ends exist in solution,[6-8] the cis form predominating in the former case at all temperatures in tetrahydrofuran. Polybutadienyllithium on the other hand at equilibrium is a mixture of the two at 0°, the cis form being favored at low temperatures. It is clear that a number of processes leading to a change in the nature of the active species can occur. All of these have been previously described as "isomerizations" although strictly speaking some are chemical reactions (e.g., polystyrylsodium[2]) and are irreversible. Some suggested changes can be more properly described as rearrangements (e.g., polyisoprenyllithium[4]) but in addition with the dienes reversible geometrical isomerization can occur. The absorption spectra of polydienyl anions under polymerization conditions are normally found to be rather broad compared with the absorption bands found for polystyryl compounds which suggests that more than one species exists in solution. Although studies of the kinetics of diene polymerization in THF have been made, it is clear that interpretation of the results is very difficult unless one knows to what species the observed rates apply. A study has been made, therefore, of the spectra of polybutadienyllithium, -sodium, and -potassium in THF as a function of reaction conditions in an attempt to elucidate some of the changes taking place.

Experimental Section

Butadiene (Phillips Research Grade) was degassed under vacuum before being condensed onto butyllithium. It was allowed to polymerize for 40 min at −10°. This procedure was repeated once more before storage in the gas phase in blackened 5-l. bulbs. The purifications of THF and styrene have been described previously.[9] Sodium tetraphenylboride (Fisher Scientific) was purified as described by Parry et al.[10] The lithium salt was prepared in the same way. Potassium triphenylcyanoboride, used because of the low solubility of the tetraphenylboride salt, was precipitated from a concentrated aqueous solution of the commercially available sodium salt (K&K Laboratories) by the addition of an equivalent amount of concentrated aqueous reagent grade potassium chloride, and subsequently recrystallized from ether–cyclohexane. The sodium content was found to be less than 0.7%.

The experimental procedures, involving breakseal techniques and greaseless high-vacuum systems, have been reported in earlier communications from these laboratories. Initiation of polymerization was attained either by contacting butadiene with the appropriate alkali-metal film or by use of the corresponding oligomeric polystyryl salt prepared in benzene and subsequently freeze dried to remove the solvent. In the former case, the solvent originally distilled into the reaction vessel from Na/K alloy was finally dried over an alkali-metal film *in situ*. This procedure was found to be