Isomeric Graft Copolymers and Interpenetrating Polymer Networks. Theory and Experiment

L. H. Sperling,* K. B. Ferguson, J. A. Manson, E. M. Corwin, and D. L. Siegfried

Materials Research Center, Lehigh University, Bethlehem, Pennsylvania 18015.

Received May 14, 1976

ABSTRACT: There are literally hundreds of distinguishable multipolymer combinations in the scientific and patent literature. For the most part, these materials are now designated as "blends" or "grafts". A possible nomenclature scheme based on ring theory is presented, along with examples. The proposed nomenclature also suggests novel chemical experiments in polymer science. As an example, the decross-linking of a simple polymer network is briefly described. Polystyrene (PS) was synthesized with acrylic acid anhydride (AAA) as a cross-linking agent. Upon soaking in ethylene diamine, the AAA bonds were broken. The resulting linear polymer had the same molecular weight as the product prepared without cross-linking agent. The relationships between the chemical steps and the ring theory nomenclature scheme are explored.

Graft copolymers ad interpenetrating polymer networks (IPN's) can be synthesized by a multiplicity of techniques; each yields a distinctive morphology and topology.[1,2] For example, the two polymers can be synthesized simultaneously or sequentially, cross-linking may be imposed during the polymerization or afterwards. In addition, the two polymers may or may not be grafted to each other. In order to describe these new materials, an improved nomenclature is required. A comprehensive nomenclature also should have suggestive qualities, in order that new or yet unrecognized materials can be brought into focus.

The present paper will continue our earlier efforts[3,4] and in particular develop the ringlike characteristics of these materials, including binary addition and multiplication notation.[5] Previously, we had developed the symbols P_i, C_i, and G_{ij} to represent the formation of the linear ith polymer, the cross-linked ith polymer, and the graft of the jth polymer onto the ith polymer, respectively, in the generalized multicomponent system. The symbols m_i, c_i, and g_i stood for the monomer i, cross-linker i, and grafting agent i, respectively. Parentheses indicated simultaneous processes, and brackets indicated materials that were synthesized separately and later mixed and/or reacted. For example:

$$[m_1P_1][m_2P_2](C_1C_2) \qquad (1)$$

represents two linear polymers synthesized separately that were blended together and then both cross-linked.[6] The above assumed that the system has some of the important characteristics of a mathematical group. Now, we cast the subject in the form of a mathematical ring, as this leads to improved insight into the nature of the combinations and their proposed nomenclature.

Two simplifications must be made: (1) the use of reactive unit symbolism will be discarded, and (2) materials that are slightly or accidently grafted will be considered as blends for the present discussion. Only systems that are intentionally or extensively grafted will be so considered.

Rings and Binary Notation

A system with ringlike characteristics has two binary operations, which in ordinary algebra are addition and multiplication. We take all binary polymer combinations not involving bonding between them as the "addition", and its binary operation will be designated o_1. Thus:

$$P_2 o_1 P_1 = M_{12} \qquad (2)$$

means a blend of polymers 1 and 2, read from right to left. (The old notation read from left to right.) In important ways the symbol o_1 replaces the brackets used earlier, which stood for blending.

The combinations involving chemical bonding between polymers will be the "multiplication", and its binary operation will be designated o_2. Thus:

$$P_1 o_2 P_1 = C_1 \qquad (3)$$

indicates a cross-linked polymer 1, and

$$P_2 o_2 P_1 = G_{12} \qquad (4)$$

indicates the grafting of polymer 2 onto a polymer 1 backbone.

The binary operation tables for these two types of operations are shown in Tables I and II. The tables are infinite in size in the general case, with very complex structures possible. Two specific points should be noted: (1) In the Blends table, the commutative law of addition holds, and $M_{12} = M_{21}$, where M stands for mixture or blend. (2) Coefficients are omitted. In general, $xP_1 o_1 yP_1 = (x + y)P_1$, etc. However, simple combinations of the two tables are more illustrative. For example:

$$P_2 o_2 (P_2 o_1 P_1) = P_2 o_2 M_{12} = C_2 o_1 G_{12} \qquad (5)$$

which makes use of the distributive property of multiplication over addition, shows some of the characteristics of the notation. It should be noted that the accidentally or slightly grafted polymer combinations fit the blend table better than the graft-cross-link table. Thus, most of the IPN's synthesized to date may be considered analogous to a blend of two cross-linked polymers (a chemical blend, not a mechanical one):

$$C_1 o_1 C_2 = I_{12} \qquad (6)$$

where I stands for an IPN.

Table I
"Addition" Table for Polymer Blends

o_1	P_1	P_2	. . .
P_1	P_1	M_{12}	
P_2	M_{21}	P_2	
⋮			

Table II
"Multiplication" Table for Cross-Linked and Grafted Systems

o_2	P_1	P_2	. . .
P_1	C_1	G_{12}	
P_2	G_{21}	C_2	
⋮			

Table III

Application of Group and Ringlike Nomenclature to Selected IPN-Related Patent Literature[a]

Author and patent No.	Group theory designation	Polymer I	Polymer II	Use	Comments	Common designation	Ringlike designation
M. J. Hatch, U.S. 3 041 292 (1962)	$(m_1c_1)(P_1C_1)m_2P_2$	Sulfonated polystyrene	Poly(acrylic acid)	Ion exchange resin	Suspension polymerization	Semi-I	$P_2o_1C_1$
T. A. Solak and J. T. Duke, U.S. 3 426 102 (1969)	$m_1P_1m_2(P_2G_{12})$	Polybutadiene	Poly(acrylonitrile-*co*-ethyl acrylate)	Impact resistant plastic	Emulsion polymerization	Graft copolymer	$P_2o_2P_1$
R. D. Hibelink and G. H. Peters, U.S. 3 657 379 (1972)	$[m_1P_1][(m_2P_2)(c_1m_3)](C_1P_3G_{23})$	Epoxy resin	Polyester resin	Adhesive	Suspension polymerization; polyester resin AB crosslinked, P_3 = polystyrene	IPN	$\begin{pmatrix}P_1\\o_1\\P_3\end{pmatrix}\begin{matrix}o_2\\ \\o_2\end{matrix}\begin{pmatrix}P_1\\o_1\\P_2\end{pmatrix}$
F. G. Hutchinson, British 1 239 701 (1971)	$(m_1c_1m_2)(P_1C_1)P_2$	Polyurethane	Poly(methyl methacrylate)	Shapable polymeric articles	Bulk polymerization	Semi-IPN	$P_2o_1C_1$
J. M. Hawkins, British 1 197 794 (1970)	$[m_1P_1][m_2P_2]C_1$	Epoxy	Polyurethane	Adhesive	Bulk polymerization	Semi-IPN	$P_1o_2\begin{pmatrix}P_1\\o_1\\P_2\end{pmatrix}$
G. S. Solt, British 728 508 (1955)	$(m_1c_1)(P_1C_1)(m_2c_2)(P_2C_2)$	Chloromethyl polystyrene	Sulfonated polystyrene	Ion exchange resin	Suspension polymerization; complex reaction scheme	IPN	$C_2o_1C_1$
W. H. Parrkiss and R. Orr, British 786 102 (1957)	$[m_1P_1(m_2c_3)P_2G_{12}][m_3P_3]C_3$	Polyester resin	Polystyrene	Flexible casting resin	P_3 = epoxy resin; bulk polymerization. Unsaturated polyester plus styrene produces AB cross-linked copolymer; two networks with three polymers	IPN	$P_3o_2P_3o_1\begin{pmatrix}P_2\\o_2\\P_1\end{pmatrix}\begin{matrix}o_2\\ \\o_2\end{matrix}\begin{pmatrix}P_1\\o_2\\P_2\end{pmatrix}$
J. J. P. Staudinger and H. M. Hutchinson, U.S. 2 539 376 (1951)	$(m_1c_1)P_1m_2P_2$	Poly(methyl methacrylate)	Poly(ethyl vinyl ketone)	Optically smooth plastic surfaces	Bulk polymerization. Some compositions IPN's	Semi-I	$P_2o_1C_1$
J. J. P. Staudinger and H. M. Hutchinson, U.S. 2 539 377 (1951)	$(m_1c_1)P_1(m_2c_2)P_2$	Polystyrene	Polystyrene	Optically smooth plastic surfaces	Bulk polymerization. Millar IPN's and Semi-I's. (Original application date in Great Britain July 23, 1941)	IPN	$C_2o_1C_1$
K. C. Frisch, H. L. Frisch, and D. Klempner, British 2 153 987 (1972)	$[m_1P_1][m_2P_2](C_1C_2)$	Polyacrylate	Polyurethane	Tough elastomeric films	Both polymers emulsion polymerized (example 1)	IPN	$\begin{pmatrix}P_1\\o_1\\P_2\end{pmatrix}\begin{matrix}o_2\\ \\o_2\end{matrix}\begin{pmatrix}P_1\\o_1\\P_2\end{pmatrix}$
	$(m_1c_1m_2c_2)(P_1P_2)$	Epoxy	Polyurethane	Tough plastic	Simultaneous polymerization (example 17)	SIN[b]	$(P_2o_2P_2o_1P_1o_2P_1)$
	$[m_1P_1m_2][m_3P_3](P_2G_{12}C_3)$	Polyester	Polystyrene	Tough plastic	P_3 = polyurethan (example 12) (three distinguishable topologies in patent)	SIN	$\begin{pmatrix}P_2\\o_1\\P_3\end{pmatrix}\begin{matrix}o_2\\ \\o_2\end{matrix}\begin{pmatrix}P_1\\o_1\\P_3\end{pmatrix}$

H. A. Clark, U.S. 3 527 842 (1970)	$[m_1P_1][m_2P_2][m_3P_3]$ $G_{23}C_1$	Polysiloxane	Polysiloxane	Pressure sensitive adhesive	P_3 = polysiloxane. Active groups: P_1 has OH, P_2 has $CH{=}CH_2$, P_3 has H, P_2 and P_3 form an AB cross-linked copolymer	IPN	$(P_1)\ o_2\begin{pmatrix}1\\o_2\\P_3\\o_1\\P_2\end{pmatrix}\begin{matrix}o_2\\ \\o_2\\ \\o_2\end{matrix}\begin{pmatrix}P_1\\o_1\\P_2\\o_1\\P_3\end{pmatrix}$
Anonymous (CIBA, Ltd.), British 1 223 338 (1971)	$m_1P_1(m_2c_1c_2)$ $(P_2C_2C_1)$	Poly(diallyl phthalate)	Epoxy	Compression molding composition	Simultaneous reactions	IPN	$\begin{pmatrix}P_1\\o_1\\C_2\end{pmatrix}\begin{matrix}o_2\\ \\o_2\end{matrix}\begin{pmatrix}P_1\\o_2\\1\end{pmatrix}$
H. L. Stephens and T. F. Reed, U.S. 3 645 940 (1972)	$[m_1P_1][m_2P_2]C_1$	SBR	Starch	Reinforced rubber	Mechanical mixing for phase inversion	Semi-IPN	$P_1o_2\begin{pmatrix}P_1\\o_1\\P_2\end{pmatrix}$
L. H. Sperling and D. A. Thomas, U.S. 3 833 404 (1974)	$(m_1c_1)(P_1C_1)(m_2c_2)$ (P_2C_2)	Poly(ethyl methacrylate)	Poly(*n*-butyl acrylate)	Noise damping coating	Emulsion polymerization with overcoat	IPN	$C_2o_1C_1$
P. Mendoyanis, U.S. 3 316 324 (1967)	$[m_1P_1c_2][m_2c_1]$ $(P_2C_2C_1)$	Polysulfide rubber	Epoxy resin	Adhesive sealant and crack filler	Components react on mixing in bulk	SIN or IPN	$\begin{pmatrix}P_1\\o_1\\C_2\end{pmatrix}\begin{matrix}o_2\\ \\o_2\end{matrix}\begin{pmatrix}P_1\\o_2\\1\end{pmatrix}$
B. Vollmert, U.S. 3 055 859 (1962)	$[m_1P_1][m_2P_2]c_1$ $(G_{12}C_1)$	Poly(butyl acrylate)	Polystyrene	Impact resistant plastic	Grafting and cross-linking in bulk postpolymerization. (example 1)	Semi-IPN	$P_1o_2(P_2o_1P_1)$
	$[m_1c_1(P_1C_1)][m_2P_2]$ $[m_3P_3][m_4P_4]$ $(G_{12}G_{13}G_{14})$	Poly(butyl acrylate)	Poly(butyl acrylate-*co*-styrene)	Impact resistant plastic	P_3 = polystyrene, P_4 = polystyrene; P_1 has carboxyl groups, P_2, P_3, and P_4 have OH, latex polymerization, mixed latex type (example 7)	Semi-IPN	$(P_4o_1P_3o_1P_2)o_2C_1$
	$[(m_1c_1)(P_1C_1)]$ $[(m_2c_2)(P_2C_2)]$ $[m_3P_3]$	Poly(*n*-butyl acrylate)	Poly(*n*-butyl acrylate-*co*-acrylonitrite)	Impact resistant plastic	P_3 = poly(styrene-*co*-acrylonitrile). Latex polymerization; polymers mixed after precipitation (example 20). This patent has 31 examples, mostly distinguishable topologies!	Two noninterpenetrating networks; a blend	$P_3o_1C_2o_1C_1$
J. H. Spilner, U.S. 3 681 475 (1972)	$(m_1c_1)(P_1C_1)(m_2c_2)$ $(P_2C_2)m_3P_3$	Butyl acrylate copolymer	Poly(butyl acrylate-*co*-*tert*-butylstyrene)	Impact resistant plastic	P_3 = poly(methyl methacrylate). Emulsion polymerization, no new particles (example 7)	IPN	$P_3o_1C_2o_1C_1$
M. Baer, U.S. 3 041 309 (1962)	$[m_1P_1m_2P_2G_{12}]$ $[m_3P_3]$	Acrylic copolymer	Methacrylic copolymer	Additive to plastics for toughening	P_3 = poly(styrene-*co*-acrylonitrile), emulsion polymerization	Graft—Blend	$P_3o_1(P_2o_2P_1)$
C. F. Ryan and R. J. Crochowski, U.S. 3 426 101 (1969)	$[(m_1c_1)(P_1C_1)(m_2c_2)$ $(P_2C_2)m_3P_3][m_4P_4]$	Poly(*n*-butyl acrylate)	Polystyrene	Impact modifier	P_3 = poly(methyl methacrylate); P_4 = poly(vinyl chloride). Latex polymerization, overcoat, blend	IPN + blend	$P_4o_1(P_3o_1C_2o_1C_1)$
J. Rosenberg, U.S. 3 928 113 (1975)	$m_1P_1(m_2c_2)(P_2C_2G_{12})$	Water soluble polymer	Polyene	Removable nail polish	Surface graft	Semi-II	$C_2o_2P_1$
D. F. Lohr, Jr., and J. K. Kang, U.S. 3 928 282 (1975)	$[m_1P_1][m_2P_2]$ $(C_1C_2G_{12}G_{21})$	Hydroformylated polybutadiene	1,2 Polybutadiene	Electrical insulation	Simultaneous grafting and cross-linking	IPN	$\begin{pmatrix}P_1\\o_2\\P_2\end{pmatrix}\begin{matrix}o_2\\ \\o_2\end{matrix}\begin{pmatrix}P_1\\o_1\\P_2\end{pmatrix}$

[a] The authors wish to thank Dr. D. Klempner for aiding in the literature search. [b] SIN stands for simultaneous interpenetrating network.

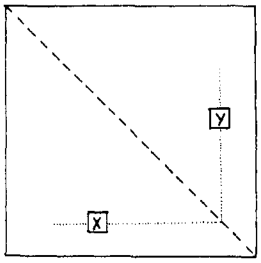


Figure 1. The function γ moves an element to its symmetric position across the diagonal. In this case, elements X and Y are interchanged.

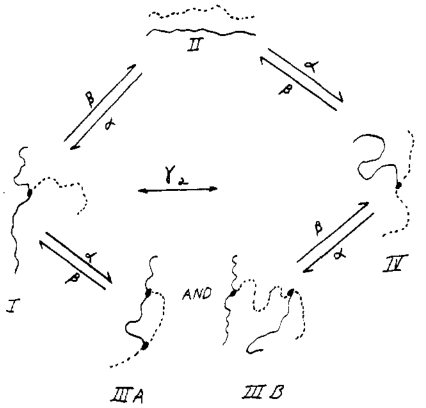


Figure 2. An illustration of the interrelations among the polymer blend and graft functions α, β, and γ.

Besides the symbols defined above, it is also convenient to introduce the semi-IPN, represented by S. A semi-IPN has one polymer cross-linked and one linear. In general, the notation $S_{ik}{}^{h}$ is a semi-IPN of polymers i and k, and h is 1 or 2, depending on whether the first or the second polymer so introduced contains the cross-links. It is obvious that much more complicated symbols could be evolved. For simplicity, however, combinations of existing symbols will be employed, as in the right-hand side of eq 5.

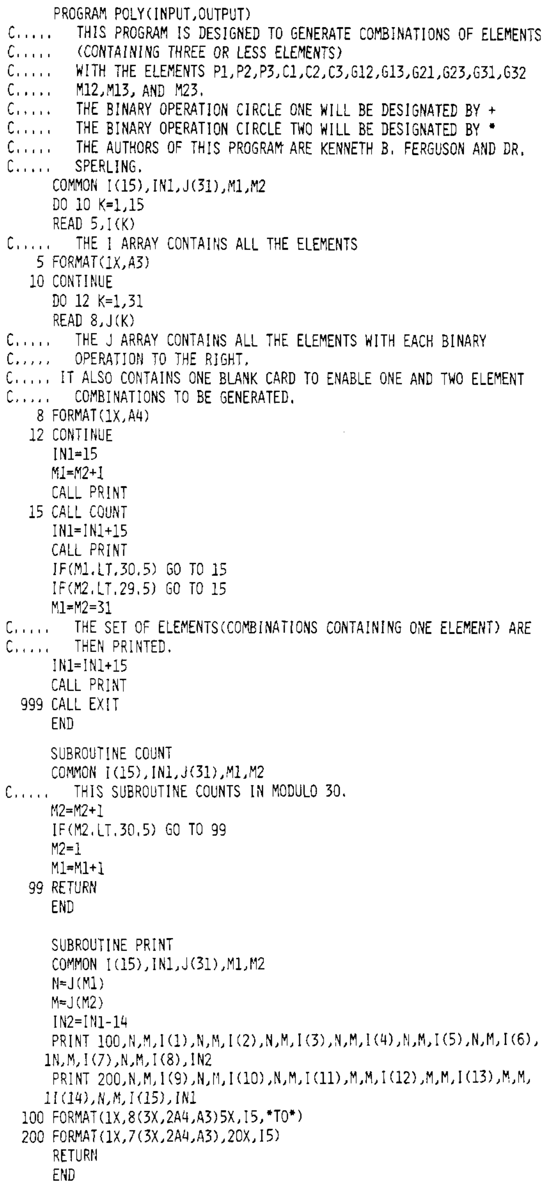
In Tables I and II, the elements in the left-hand column are employed first and are "multiplied" by the elements in the top row. This specifies the time order of the operations. Upon examination of the tables, a striking symmetry becomes apparent. Elements on either side of the diagonal running from the upper left to the lower right are clearly related. For example, the qualitative relationship between G_{12} and G_{21} is obvious, but now we observe that they are quantitatively related in Table II, lying in symmetric positions across the diagonal. In fact, a function, γ, may be defined which will cause the element to be moved to its corresponding position across the diagonal and physically adopt its new structure. In general, there are two γ functions: γ_1 for the blends, Table I, and γ_2 for the grafts and cross-links, Table II. The transformation of element X into element Y by the function γ is shown in Figure 1. Thus:

$$\gamma_2 G_{12} = G_{21} \tag{7}$$

γ_2 transforms G_{12} to G_{21} within graft-cross-link Table II.

Since the patent literature contains numerous multipolymer systems, some of those relating to IPN's and IPN-like materials are abstracted in Table III. This table shows both the new and the old notation. Also included are more complex notations, such as

$$\begin{pmatrix} P_2 \\ o_2 \\ P_1 \end{pmatrix} \begin{matrix} o_1 \\ \\ o_2 \end{matrix} \begin{pmatrix} P_1 \\ o_2 \\ P_2 \end{pmatrix} \tag{8}$$



```
      PROGRAM POLY(INPUT,OUTPUT)
C.....   THIS PROGRAM IS DESIGNED TO GENERATE COMBINATIONS OF ELEMENTS
C.....   (CONTAINING THREE OR LESS ELEMENTS)
C.....   WITH THE ELEMENTS P1,P2,P3,C1,C2,C3,G12,G13,G21,G23,G31,G32
C.....   M12,M13, AND M23.
C.....   THE BINARY OPERATION CIRCLE ONE WILL BE DESIGNATED BY +
C.....   THE BINARY OPERATION CIRCLE TWO WILL BE DESIGNATED BY *
C.....   THE AUTHORS OF THIS PROGRAM ARE KENNETH B. FERGUSON AND DR.
C.....   SPERLING.
      COMMON I(15),IN1,J(31),M1,M2
      DO 10 K=1,15
      READ 5,I(K)
C.....   THE I ARRAY CONTAINS ALL THE ELEMENTS
    5 FORMAT(1X,A3)
   10 CONTINUE
      DO 12 K=1,31
      READ 8,J(K)
C.....   THE J ARRAY CONTAINS ALL THE ELEMENTS WITH EACH BINARY
C.....   OPERATION TO THE RIGHT.
C..... IT ALSO CONTAINS ONE BLANK CARD TO ENABLE ONE AND TWO ELEMENT
C.....   COMBINATIONS TO BE GENERATED.
    8 FORMAT(1X,A4)
   12 CONTINUE
      IN1=15
      M1=M2+1
      CALL PRINT
   15 CALL COUNT
      IN1=IN1+15
      CALL PRINT
      IF(M1.LT.30.5) GO TO 15
      IF(M2.LT.29.5) GO TO 15
      M1=M2=31
C.....   THE SET OF ELEMENTS(COMBINATIONS CONTAINING ONE ELEMENT) ARE
C.....   THEN PRINTED.
      IN1=IN1+15
      CALL PRINT
  999 CALL EXIT
      END

      SUBROUTINE COUNT
      COMMON I(15),IN1,J(31),M1,M2
C.....   THIS SUBROUTINE COUNTS IN MODULO 30.
      M2=M2+1
      IF(M2.LT.30.5) GO TO 99
      M2=1
      M1=M1+1
   99 RETURN
      END

      SUBROUTINE PRINT
      COMMON I(15),IN1,J(31),M1,M2
      N=J(M1)
      M=J(M2)
      IN2=IN1-14
      PRINT 100,N,M,I(1),N,M,I(2),N,M,I(3),N,M,I(4),N,M,I(5),N,M,I(6),
     1N,M,I(7),N,M,I(8),IN2
      PRINT 200,N,M,I(9),N,M,I(10),N,M,I(11),M,M,I(12),M,M,I(13),M,M,
     1I(14),N,M,I(15),IN1
  100 FORMAT(1X,8(3X,2A4,A3)5X,I5,*TO*)
  200 FORMAT(1X,7(3X,2A4,A3),20X,I5)
      RETURN
      END
```

Figure 3. Ring-like combination by computer programming.

Equation 8 is read both vertically and horizontally, with time sequences moving from right to left. Quantities within the parentheses are taken simultaneously. Equation 8 permits a fair (but still not entirely complete) representation of an AB-cross-linked copolymer,[7] as distinguished from the simple graft copolymer analogue, which does not constitute a network.

Limitations of the Ringlike Format

The system described above does not fulfill all of the formal requirements for a ring. Examination of the theorems in Chapter 2 of McCoy's book[5] reveals both useful and apparently applicable theorems for the present case and also some important nonapplicable theorems.

For an example of an applicable theorem (McCoy's theorem 2.6), "If a and b are elements of a ring R, the equation $a o_1 X = b$ has in R the unique solution $X = b o_1(-a)$." In this case, $-a$ serves as an inverse. The inverse quantities also show the limitations of the ringlike characteristics, however. For example:

$$(-P_2)o_2P_1 \neq -(P_2o_2P_1) \tag{9}$$

While the addition and multiplication table have a zero and a unity, respectively, these quantities are not transferable between the two sets of binary operations. While inverses should be considered real, obviously negative algebraic quantities (such as inverses alone) lead to imaginary physical quantities. Until the special theorems relating to the present case are worked out, the readers sense of possible chemical operations must prevail.

Decross-Linking and Degrafting

A more important aspect involves the concepts of decross-linking and degrafting. The symbol ($-G_{12}$) implies removal of both polymers and the graft site. What is really needed is a symbol to change from one binary table to the other, as a degrafted polymer becomes a blend. To meet this need, we define two functions, α and β, which move combinations of elements from the o_1 table to the o_2 table, and vice versa, respectively. For example:

$$\alpha M_{12} = \alpha(P_2 o_1 P_1) = P_2 o_2 P_1 = G_{12} \tag{10}$$

$$\beta G_{12} = \beta(P_2 o_2 P_1) = P_2 o_1 P_1 = M_{12} \tag{11}$$

$$\beta C_1 = \beta(P_1 o_2 P_1) = P_1 o_1 P_1 = P_1 \tag{12}$$

Equation 12 yields $2P_1$, or just P_1 in the sense of Table I, omitting the coefficient.

The relationships among α, β, and γ may be seen more clearly with the aid of Figure 2. In Figure 2 are shown ways in which two polymers may be grafted, degrafted, and regrafted. While structure I must go through either II or III to reach IV from a chemical point of view, the effect is to apply the function γ_2 in a conceptual way to go directly from structure I to structure IV.

Systematic Evolution of Possible Combinations

Noting that binary operations o_1 and o_2 bear a simple analogy to additon and multiplication algebraic operations, it was desired to develop a computer program to systematically evolve and number combinations specified by certain rules. One such program is shown in Figure 3, which reads out all combinations of one, two, and three elements.

The number of combinations generated was a function of the number of elements allowed to combine, as shown in Table IV. Inclusion of all combinations requires a summation. For example, all combinations of one, two, and three elements is 15 + 450 + 13 500 = 13 965.

The numbering of the combinations is useful for nomenclature purposes. The general rules for going back and forth between the physical combinations and their corresponding base 10 numbers are shown in Appendix II. The procedure calls forth memories of the joke about joke numbers, where the joke number not heard before is funniest; in this case, here-to-fore unknown combinations are thus called into being and await being made.

The physical combinations are reduced to a modulo 10 number via an intermediate step which requires the use of Table V. Table V numbers the basic elements and the combinations of the elements and an associated operation. Three polymers and their various cross-linked, grafted, and blended combinations are specified. Table VI gives examples of encoding and decoding.

Clearly the combinations specified by the present computer program are limited to those capable of being represented on one horizontal line and do not include the two-dimensional arrays developed in Table III. Also, parentheses are omitted for simplicity, and of course the combinations are limited by the kinds of elements introduced. (In particular, the S and I elements are omitted from the program, although many of the combinations of basic elements generate S and I topologies.) The more general cases obviously would have many more combinations than specified by Table IV.

Table IV
Theoretical Number of Combinations

No. of elements in combination	No. of different combinations possible
1	15
2	450
3	13 500
4	405 000
5	12 150 000
6	364 500 000
7	10 935 000 000

Table V
Numerical Combinations for Encoding and Decoding

Initial polymer elements		Polymer elements under o_1 and o_2			
N_1	Nomenclature symbol	N_2, N_3, etc.	Nomenclature symbols	N_2, N_3 etc.	Nomenclature symbols
1	P_1	0	P_1o_1	15	P_1o_2
2	P_2	1	P_2o_1	16	P_2o_2
3	P_3	2	P_3o_1	17	P_3o_2
4	C_1	3	C_1o_1	18	C_1o_2
5	C_2	4	C_2o_1	19	C_2o_2
6	C_3	5	C_3o_1	20	C_3o_2
7	G_{12}	6	$G_{12}o_1$	21	$G_{12}o_2$
8	G_{13}	7	$G_{13}o_1$	22	$G_{13}o_2$
9	G_{21}	8	$G_{21}o_1$	23	$G_{21}o_2$
10	G_{23}	9	$G_{23}o_1$	24	$G_{23}o_2$
11	G_{31}	10	$G_{31}o_1$	25	$G_{31}o_2$
12	G_{32}	11	$G_{32}o_1$	26	$G_{32}o_2$
13	M_{12}	12	$M_{12}o_1$	27	$M_{12}o_2$
14	M_{13}	13	$M_{13}o_1$	28	$M_{13}o_2$
15	M_{23}	14	$M_{23}o_1$	29	$M_{23}o_2$
				30	blank

Table VI
Examples of Encoding and Decoding for Two and Three Element Combinations

Physical combination	Modulo 30–30–15	Modulo 10
$P_3o_2G_{23}o_2M_{13}$	17–24–14	08024
$M_{12}o_1G_{21}o_2G_{12}$	12–23–7	05752
$G_{21}o_1G_{12}o_1M_{13}$	8–6–14	03704
$G_{23}o_1G_{13}o_1P_2$	9–7–2	04157
$M_{23}o_1G_{21}o_1M_{12}$	14–8–13	06433
$C_3o_1G_{31}o_1G_{23}$	5–10–10	02410
$C_1o_2C_2o_2G_{32}$	18–19–12	08397
$G_{21}o_2M_{23}o_2M_{13}$	23–29–14	10799
$M_{23}o_2G_{31}o_2G_{13}$	14–25–8	06683
$M_{23}o_2P_3$	30–29–3	13928

Decross-Linking of Polystyrene Networks

Experiments both in the field of grafting and degrafting and cross-linking and decross-linking are in progress in this laboratory, making use of the concepts developed above. As a simple example of eq 12, the decross-linking of a polystyrene network is presented below.

1. Styrene and styrene containing 0.2% w/w acrylic acid anhydride (AAA) were thermally polymerized in bulk under similar conditions.

2. The two samples were placed in contact with toluene. The non-AAA containing sample dissolved, while the AAA-containing sample swelled approximately ten times its initial volume.

This indicates that the AAA introduced chemical cross-linking.

3. After soaking the cross-linked sample in ethylene diamine, it was found that the sample dissolved in toluene. This indicates that the ethylenediamine caused the hydrolysis of the acid anhydride bond.

Table VII
Polystyrene Molecular Weights

Polymer	M_v, g/mol
Linear polystyrene	3.3×10^5
PS with AAA, hydrolyzed	3.2×10^5

Table VIII
Molecular Weight of Chain Segments between Cross-Links[a]

Method	V_2	M_c, g/mol
Weight increase	0.0802	1.1×10^5
Length increase	0.102	4.5×10^4
Calculated		3.4×10^4[a]

[a] Infinite chain length assumed.

4. The intrinsic viscosities of the two dissolved polymers were determined, and M_v was calculated for both polymers using the Mark-Houwink relationship ($[\eta] = KM^a$), with constants from the Polymer Handbook.[8] The results are show in Table VII.

These results, identical within experimental error, indicate that the original polymerization kinetics were not significantly affected by the presence of the AAA, except to introduce cross-linking.

5. The Flory–Rehner equation was employed to estimate M_c, the molecular weight of the subchains between cross-links.

Based on the increase in weight of the swollen sample, v_2 was found to be 0.0802. Based on the increase in length, $v_2 = 0.102$. Using $X = 0.47$, the M_c values were then estimated and compared with the values calculated from the known addition of AAA. See Table VIII.

Reasonable agreement (at least in order of magnitude) was obtained, in view of the precision and accuracy inherent in the measurements and calculations.

6. Probably the "weight increase" technique above is more accurate than the "length increase" method. However, the cross-link levels were very low, making accurate assessments via the Flory–Rehner equation difficult.

7. Ordinarily, the swelling method yields values for M_c *smaller* than those estimated from organic syntheses proportions, because of the presence of physical cross-links (i.e., chain entanglements). The inverted situation suggests that either the AAA is inefficient (resulting in dangling unreacted groups, or both vinyls being incorporated in the same chain) or that some of the anhydride bonds were hydrolyzed before the final measurements. Hydrolysis is the more probable cause.

Discussion

The current literature is very rich in combinations of two or more polymers.[9-24] While naturally the scientific literature gives more insight into the chemical and physical processes involved, a review of the patent literature often reveals far more complicated structures. In addition to the patents described in Table III, other patents may be cited.[25-42] Examination of a recent issue of the Patent Gazette revealed 18 patents on multipolymer combinations. Many of these had one or more polymers in the cross-linked state.

Classical organic and inorganic chemistry has developed an enormously complex nomenclature; a description of the fruits of modern chemical research would be impossible without it. The hundreds of different multipolymer combinations now merely described as "blends" or "grafts" show the need for improvements in the nomenclature.

The present work is not complete. Block copolymers are not described, and a few structures such as the AB cross-linked copolymers are only poorly described. While the group theory notation previously employed gave more detail, the use of the ringlike notation yields greater versatility and enhances algebraic manipulation.

The authors would appreciate comments from the readers relating to errors, inconsistencies, or possible improvements in the proposed nomenclature.

Acknowledgment. The authors are pleased to acknowledge the support of Grant AFOSR-76-2945 and Wright-Patterson AFB Contract No. F33615-75-C-5167. The authors also wish to thank Dr. C. S. Queen for his many helpful discussions.

Appendix I

In a computer program used to generate all the combinations possible for a particular system, two variables must be specified. These two variables are (1) the binary operations to be used, in our study it was o_1 and o_2, and (2) the number of elements in the system such as P_1, C_2, G_{23}, M_{13}, etc. Once these are specified the writing of a program is a simple matter. The program should count in a modulo equal to the number of elements times the number of operations.

First data arrays are read in. All the elements are read in under an alphanumeric format, then all the elements with each binary operation to the right of it are read into the computer followed by a blank card.

Next various counters are initialized and the first set of combinations are printed out, then the counters are incremented in their respective modulo and these results are printed. This is repeated until all values are printed.

The program employed is in Figure 3.

Appendix II

Rules for Encoding and Decoding Physical Combinations to and from Base Ten (General Case).

I. From a Base Ten Number to Physical Nomenclature.

Step 1. Identify the number of elements in the combination (duplicates count) and designate this as *i*. Examples:

$$P_1o_1P_2o_2P_3 \qquad i = 3$$

$$P_1o_1P_1o_2P_2 \qquad i = 3$$

Step 2. If $i = 2$ go to step 7.

Step 3. Divide base ten number by $(30^{(i-2)} \times 15)$.

Step 4. Designate Ni as the number to the left of the decimal point.

Step 5. Subtract $Ni \times (30^{i-2}) \times 15$ from the base ten number and designate this as the new base ten number.

Step 6. $i = i - 1$, go to step 2.

Step 7. Divide base ten number by 15.

Step 8. Designate $N2$ as the number to the left of the decimal point.

Step 9. Subtract $N2 \times 15$ from the base ten number.

Step 10. Designate this number as $N1$.

Step 11. If $N1 = 0$, then $N2 = N2 - 1$ and then $N1 = 15$.

Step 12. Using Table V convert $N1$, $N2$, . . . , Ni to nomenclature symbols.

Step 13. Write combination right to left starting with $N1$ and ending with Ni.

II. Physical Nomenclature to Base Ten Number.

Step 1. Identify polymer numbers $N1, N2, N3, \ldots, Ni$ using Table V.

Step 2. Base ten number is given by the formula:

$$N_{10} = \left(\sum_{j=3}^{i} (Nj) \times 30^{(j-2)} \times 15\right) + (N2 \times 15) + N1$$

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Small-Angle X-Ray Scattering from Block Copolymers

G. G. Vitale and D. G. LeGrand*

General Electric Company, Corporate Research and Development Center,
Synthesis and Characterization Branch, Chemical Laboratory,
Schenectady, New York 12301.

Received August 18, 1975

ABSTRACT: Debye's theory of scattering from dilute solutions of homopolymer coils and rods is extended to block copolymers. The angular dependence of scattering is dependent (1) on the electron density difference between the solvent and the different blocks in the molecule, (2) on structure, and (3) on conformation. Results indicate that small-angle x-ray data from solutions made with appropriate solvents should provide information about copolymer structure.

Recent advances in polymer technology have made possible the synthesis of a large variety of block and graft copolymers. During the past several years, many of the properties of silicone-containing alternating block copolymers have been studied in our laboratories[1-3] to determine the feasibility of designing materials to meet specific needs. Characterization of these materials by viscometry, osmometry, and NMR proved inadequate because copolymer physical properties were found to be dependent not only on their composition and molecular weight but also on their molecular structure and the larger inter- and intramolecular structures which they form.

In an attempt to overcome this deficiency, we have used small-angle x-ray scattering (SAXS) as a tool to study the structure of copolymers in the bulk and swollen states and have initiated studies in solution to further characterize these materials and to understand their properties.[4-6] Previous workers have treated scattering from copolymers, but in the light-scattering region, so that the scattering due to the polymer's structure has not been important. In many cases, the molecule is then treated like a homogeneous particle whose refractive index and refractive index increment are weighted averages of the values for the two homopolymers.[7] Benoit et al.[8-11] have treated copolymer scattering in greater detail, even deriving structure-dependent expressions for several simple copolymer molecules.

Because many different models can account for similar scattering phenomena, other techniques must supplement SAXS data in order to confirm any proposed model. It is the objective of this paper to propose and analyze a model which might be used to interpret data from dilute solutions of coils or rigid rods. We assume that the alternating block copolymer molecule is monodisperse in structure, composition, and molecular weight and consists of alternating A and B blocks. Extension of the work to polydisperse material is currently under investigation and will be reported later.

Scattering from Copolymer Solutions. We consider a small volume in which we suppose a single copolymer molecule, N units long, can be found. The intensity of x-ray scattering by this molecule will be dependent upon its size, shape, composition, and the electron density difference between the various species within the molecule and their surroundings.