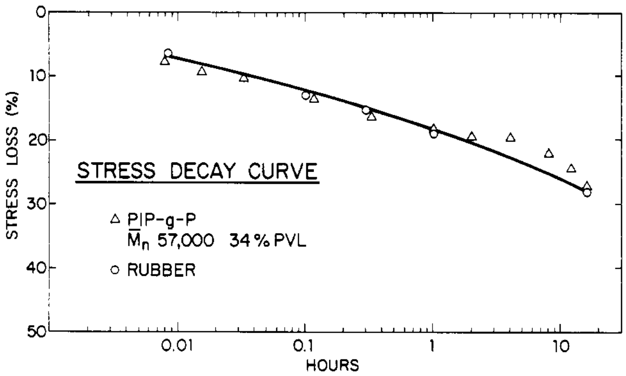

Figure 3.

period than that of strips of a sulfur-cured gum natural rubber. These data together with resilience and stress–strain behavior indicate that the crystalline cross-links in oriented ABA-*g*-A block–graft copolymers of pivalolactone and isoprene are as effective as are the chemical cross-links.

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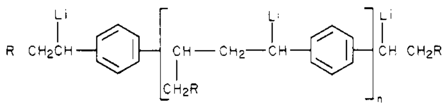

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Graph Theory and Molecular Distribution. 2. Copolycondensation of A-Group Polyfunctional Monomers with B-Group Polyfunctional Monomers

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ABSTRACT: The development in part 1, based on graph theory, is extended to the derivation of distribution functions for systems composed of different monomers bearing A-functional groups together with different monomers bearing B-functional groups (systems of order II); the A group can react only with the B group and vice versa. These distribution functions are identical with those established by Stockmayer, using generating functions.

Some years ago, in order to examine cases more general than those dealt with in previous studies,[1-6] Stockmayer[7,8] proposed a generalized distribution function for a variety of monomers bearing A-functional groups which can only react with a variety of monomers bearing B-functional groups (systems of order II[9]). The calculations involved in establishing this distribution function are tedious, particularly in the determination of Lagrangean multipliers.

Later on, Gordon and co-workers[10,11] showed that the distribution function could be calculated by using the theory of stochastic branching processes.[12] But this technique involves abstract mathematics and requires deriving probability generating functions; the method is quite general but rather difficult to use.

In the preceding paper,[13] we showed how graph theory allows one to obtain directly and readily the molecular distribution functions in the most general system of order I,[9] i.e., consisting of various monomer units with different functionalities, all sites being identical and equireactive. The purpose of this paper is to establish general molecular distribution functions in the case of order II systems by the same methods.

System Model

Consider a general system of order II[9] initially composed of M moles of monomers partitioned in A moles of A monomers (i.e., monomers bearing only functional groups A) and B moles of B monomers (i.e., monomers bearing only functional groups B). This type partition of the original chemical system may be characterized by the vector **M**:

$$\mathbf{M} = [A,B] \qquad M = A + B \tag{1}$$

Each of these classes of monomers may be composed of different kinds of monomers characterized by type partitions given by the vectors **A** and **B**

$$\mathbf{A} = [A_1,A_2,\ldots,A_i,\ldots,A_n] \qquad \sum_{i=1}^{n} A_i = A \tag{2}$$

$$\mathbf{B} = [B_1,B_2,\ldots,B_j,\ldots,B_m] \qquad \sum_{j=1}^{m} B_j = B \tag{3}$$

where A_i (B_j) is the number of moles of monomers of type A_i (B_j). Furthermore, let f_{A_i} (f_{B_j}) be the functionality of monomers of type A_i(B_j). Note that different types of monomers may have the same functionality, so that they differ in their chemical structure.

The study of systems composed of mixed monomers, i.e., monomers endowed with both functional groups A and B, will be dealt with in another paper.

Let ρ_{A_i} be the fraction of sites A belonging to monomers A_i, let ρ_{B_j} be the fraction of sites B belonging to monomers B_j, and let r be the stoichiometric ratio of the number of sites A to the number of sites B.

$$\rho_{A_i} = A_i f_{A_i} / \sum_{i=1}^{n} A_i f_{A_i} \tag{4}$$

$$\rho_{B_j} = B_j f_{B_j} / \sum_{j=1}^{m} B_j f_{B_j} \tag{5}$$

$$r = \sum_{i=1}^{n} A_i f_{A_i} / \sum_{j=1}^{m} B_j f_{B_j} \tag{6}$$

The number average functionalities of A monomers and B monomers are respectively $\bar{\varphi}_{0A}$ and $\bar{\varphi}_{0B}$:

$$\bar{\varphi}_{0A} = \frac{\sum_{i=1}^{n} A_i f_{A_i}}{\sum_{i=1}^{n} A_i} = \frac{\sum_{i=1} A_i f_{A_i}}{A} = \left(\sum_{i=1}^{n} \frac{\rho_{A_i}}{f_{A_i}} \right)^{-1} \tag{7}$$

$$\bar{\varphi}_{0B} = \frac{\sum_{j=1}^{m} B_j f_{B_j}}{\sum_{j=1}^{m} B_j} = \frac{\sum_{j=1}^{m} B_j f_{B_j}}{B} = \left(\sum_{j=1}^{m} \frac{\rho_{B_j}}{f_{B_j}} \right)^{-1} \tag{8}$$

In order to represent the chemical system, we will extend the model of a molecular forest developed by Gordon for the case of f-functional polycondensation[14] and used already by us, in the study of order I systems.[13]

The partition of monomers into two classes will be translated on the graph by the coloration of vertices in color "a" or "b" according to the class of the monomers which they represent.

In the original chemical system, an A_i monomer (i.e., monomer of type A_i) of functionality f_{A_i} will be depicted by a molecular graph which is a tree with a point colored in color "a" of degree f_{A_i}, called an A node, and f_{A_i} points colored in color "b" of degree 1, called B terminals. In the case we a B_j monomer, we shall have the complementary situation, i.e., a "b" colored point of degree f_{B_j} (B node) linked to f_{B_j} "a" colored points of degree 1 (A terminals). In this paper, we will assume that the node may be a point of any degree ≥ 1.

Figure 1 shows the tree-like model of some A and B monomers. In the original chemical system, the number of A terminals is equal to the number of reactive chemical sites of type B, and the number of B terminals is equal to the number of reactive chemical sites of type A.

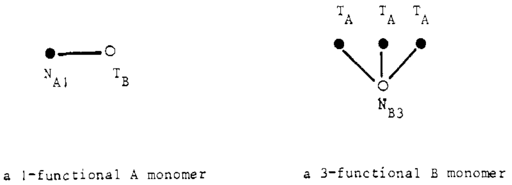

Figure 1. Schematic representation of some monomers.

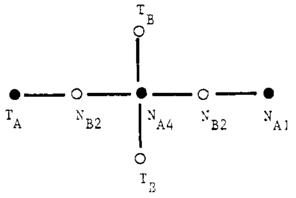

Figure 2. Schematic representation of a 4-mer composed of a 1-functional A monomer, a 4-functional A monomer, and two 2-functional B monomers.

During the evolution of the system by chemical reactions between sites A and B, links establish themselves between the A monomers and the B monomers.

Figure 2 shows an example of 4-mer composed of a 1-functional A monomer, a 4-functional A monomer, and two 2-functional B monomers.

With the assumptions that all of the sites are equireactive and intramolecular reactions do not occur on the finite molecules, then all of the latter can be represented by trees. Before the gel point, all of the molecules have tree-like structures, but after the gel point, only the sol fraction contains such molecules. In this study, we give the distribution functions for finite molecules, i.e., molecules having tree-like structures.

The degree of advancement (or conversion) may be measured by the fraction p_A of the A sites which have reacted (i.e., the fraction of all A terminals that have been eliminated by chemical link formation) or the fraction p_B of the B sites which have reacted (i.e., the fraction of all B terminals that have been eliminated by chemical link formation) with the relation between these two quantities

$$p_B = r p_A \tag{9}$$

Tree Enumeration

A. Generalities. In this part, we shall extend different fundamental tree enumeration theorems given in our first paper[13] to colored trees and especially to colored, rooted, ordered trees. Indeed, as Gordon said,[18] the number of distinct rooted, ordered trees, which can be obtained by choosing various points as roots and by ordering the branches in the half-plane in various ways, is found to be a very convenient concept for the combinatorial problems in chemistry.

By definition, we shall call a bicolored graph any graph with points having been partitioned into two sets so that adjacent points are always in different sets.

Consider now a bicolored tree having its points partitioned into two sets A and B defined by vector **s**:

$$\mathbf{s} = [s_A,s_B] \qquad s = s_A + s_B \tag{10}$$

where s_A is the number of A points, i.e., the points of color "a", and s_B is the number of B points, i.e., points of color "b".

Moreover, each of two sets of points is also characterized by type partitions given by the vectors $\mathbf{s}_A$ and $\mathbf{s}_B$:

$$\mathbf{s}_A = [s_{A_1},s_{A_2},\ldots,s_{A_i},\ldots,s_{A_n}] \qquad s_A = \sum_{i=1}^{n} s_{A_i} \tag{11}$$

$$\mathbf{s}_{\mathrm{B}} = [s_{\mathrm{B}_1}, s_{\mathrm{B}_2}, \ldots, s_{\mathrm{B}_j}, \ldots, s_{\mathrm{B}_m}] \qquad s_{\mathrm{B}} = \sum_{j=1}^{m} s_{\mathrm{B}_j} \tag{12}$$

where s_{A_i} (s_{B_j}) is the number of points of type A_i (B_j) and f_{A_i} (f_{B_j}) is the degree of the points of type A_i (B_j). Points of the same degree may be assigned to different types, but the converse is not true.

We afix the same label to vertices of the same type, so that two vertices of different types do not have the same label.

Consider a given tree having the above characteristics; we call G its automorphism group. In this paper, when we say automorphism, it is the automorphism of the graph, preserving the colors and the types of vertices. $|G|$ represents the order of the automorphism group, i.e., the number of distinct ways in which the tree can be superposed upon itself preserving the type labels.

Two nonisomorphic trees are called "isomers", and I will be the number of isomers for a given $\mathbf{s}$. We shall refer, as in our first paper,[13] to the ith such isomer simply as the ith s-mer.

B. Preliminary Remarks. Before giving the fundamental theorems, it is useful to know some relations which link the numbers of vertices and the edges in such trees.

If a is the number of edges, we have:

$$a = s - 1 = s_{\mathrm{A}} + s_{\mathrm{B}} - 1 \tag{13}$$

and

$$a = \sum_{i=1}^{n} s_{\mathrm{A}_i} f_{\mathrm{A}i} = \sum_{j=1}^{m} s_{\mathrm{B}_j} f_{\mathrm{B}_j} \tag{14}$$

From relations 13 and 14, we obtain:

$$\sum_{i=1}^{n} s_{\mathrm{A}_i}(f_{\mathrm{A}_i} - 1) = s_{\mathrm{B}} - 1 \tag{15}$$

$$\sum_{j=1}^{m} s_{\mathrm{B}_j}(f_{\mathrm{B}_j} - 1) = s_{\mathrm{A}} - 1 \tag{16}$$

C. Fundamental Theorems. Theorem 1.[16] The number of distinct ordered, rooted trees $T^{(i)}_{s,\mathrm{A}_k}$ which are rooted on a vertex of type A_k and are isomorphic with the given tree is:

$$T^{(i)}_{s,\mathrm{A}_k} = \frac{1}{|G_i|} s_{\mathrm{A}_k} f_{\mathrm{A}_k} \prod_{i=1}^{n} [(f_{\mathrm{A}_i} - 1)!]^{s_{\mathrm{A}^i}} \prod_{j=1}^{m} [(f_{\mathrm{B}_j} - 1)!]^{s_{\mathrm{B}^j}} \tag{17}$$

$$T^{(i)}_{s,\mathrm{A}_k} = \frac{1}{|G_i|} s_{\mathrm{A}_k} f_{\mathrm{A}_k} \frac{\mathcal{F}}{\mathcal{P}} \tag{18}$$

where $\mathcal{F} = \mathcal{F}_{\mathrm{A}}\mathcal{F}_{\mathrm{B}}$ and $\mathcal{P} = \mathcal{P}_{\mathrm{A}}\mathcal{P}_{\mathrm{B}}$ with

$$\mathcal{F}_{\mathrm{A}} = \prod_{i=1}^{n} [f_{\mathrm{A}_i}!]^{s_{\mathrm{A}^i}} \qquad \mathcal{F}_{\mathrm{B}} = \prod_{j=1}^{m} [f_{\mathrm{B}_j}!]^{s_{\mathrm{B}^j}}$$

$$\mathcal{P}_{\mathrm{A}} = \prod_{i=1}^{n} [f_{\mathrm{A}_i}]^{s_{\mathrm{A}^i}} \qquad \mathcal{P}_{\mathrm{B}} = \prod_{j=1}^{m} [f_{\mathrm{B}_j}]^{s_{\mathrm{B}^j}}$$

In the same way, the number of distinct ordered trees $T^{(i)}_{s,\mathrm{B}_l}$ which are rooted on a vertex of type B_l is:

$$T^{(i)}_{s,\mathrm{B}_l} = \frac{1}{|G_i|} s_{\mathrm{B}_l} f_{\mathrm{B}_l} \frac{\mathcal{F}}{\mathcal{P}} \tag{19}$$

Note also the relations:

$$\frac{T^{(i)}_{s,\mathrm{A}_k}}{s_{\mathrm{A}_k} f_{\mathrm{A}_k}} = \frac{T^{(i)}_{s,\mathrm{A}_{k'}}}{s_{\mathrm{A}_{k'}} f_{\mathrm{A}_{k'}}} = \ldots = \frac{T^{(i)}_{s,\mathrm{B}_l}}{s_{\mathrm{B}_l} f_{\mathrm{B}_l}} = \frac{T^{(i)}_{s,\mathrm{B}_{l'}}}{s_{\mathrm{B}_{l'}} f_{\mathrm{B}_{l'}}} = \ldots \tag{20}$$

The summation over the degrees of all the s_{A} vertices gives us the number of distinct ordered trees rooted on an A vertex which are isomorphic with the given tree.

$$T^{(i)}_{s,\mathrm{A}} = \frac{1}{|G_i|} \sum_{k=1}^{n} s_{\mathrm{A}_k} f_{\mathrm{A}_k} \frac{\mathcal{F}}{\mathcal{P}} = \frac{1}{|G_i|} a \frac{\mathcal{F}}{\mathcal{P}} \tag{21}$$

In the same way, for the ordered trees rooted on a B vertex, we have:

$$T^{(i)}_{s,\mathrm{B}} = \frac{1}{|G_i|} \sum_{l=1}^{m} s_{\mathrm{B}_l} f_{\mathrm{B}_l} \frac{\mathcal{F}}{\mathcal{P}} = \frac{1}{|G_i|} a \frac{\mathcal{F}}{\mathcal{P}} \tag{22}$$

We have obviously

$$T^{(i)}_{s,\mathrm{A}} = T^{(i)}_{s,\mathrm{B}} \tag{23}$$

And the number of distinct ordered rooted trees which are isomorphic with the given tree is:

$$T^{(i)}_{s} = T^{(i)}_{s,\mathrm{A}} + T^{(i)}_{s,\mathrm{B}} = \frac{1}{|G_i|} 2a \frac{\mathcal{F}}{\mathcal{P}} \tag{24}$$

The total number of distinct rooted ordered trees of all isomers of an s tree which are rooted on a vertex of type A_k is:

$$T_{s,\mathrm{A}_k} = \sum_{i=1}^{I} T^{(i)}_{s,\mathrm{A}_k} = s_{\mathrm{A}_k} f_{\mathrm{A}_k} \frac{\mathcal{F}}{\mathcal{P}} \sum_{i=1}^{I} |G_i|^{-1} \tag{25}$$

In the same way:

$$T_{s,\mathrm{B}_l} = \sum_{i=1}^{I} T^{(i)}_{s,\mathrm{B}_l} = s_{\mathrm{B}_l} f_{\mathrm{B}_l} \frac{\mathcal{F}}{\mathcal{P}} \sum_{i=1}^{I} |G_i|^{-1} \tag{26}$$

and for the total number of distinct rooted ordered trees of all isomers of an s tree rooted on an A vertex

$$T_{s,\mathrm{A}} = \sum_{i=1}^{I} T^{(i)}_{s,\mathrm{A}} = a \frac{\mathcal{F}}{\mathcal{P}} \sum_{i=1}^{I} |G_i|^{-1} \tag{27}$$

and rooted on a B vertex

$$T_{s,\mathrm{B}} = \sum_{i=1}^{I} T^{(i)}_{s,\mathrm{B}} = T_{s,\mathrm{A}} \tag{28}$$

because of relation 23, and rooted on any vertex of any type

$$T_s = T_{s,\mathrm{A}} + T_{s,\mathrm{B}} = 2a \frac{\mathcal{F}}{\mathcal{P}} \sum_{i=1}^{I} |G_i|^{-1} \tag{29}$$

By eliminating $\sum_{i=1}^{I} |G_i|^{-1}$ between the above expressions, we obtain the relations:

$$T_{s,\mathrm{A}_k} = T_{s,\mathrm{A}} \frac{s_{\mathrm{A}_k} f_{\mathrm{A}_k}}{a} = T_s \frac{s_{\mathrm{A}_k} f_{\mathrm{A}_k}}{2a} \tag{30}$$

$$T_{s,\mathrm{B}_l} = T_{s,\mathrm{B}} \frac{s_{\mathrm{B}_l} f_{\mathrm{B}_l}}{a} = T_s \frac{s_{\mathrm{B}_l} f_{\mathrm{B}_l}}{2a} \tag{31}$$

To determine $T_{s,\mathrm{A}}$, $T_{s,\mathrm{B}}$, and T_s one must know $\sum_{i=1}^{I} |G_i|^{-1}$. As in our preceding study on the order I systems,[13] we calculate $\sum_{i=1}^{I} |G_i|^{-1}$ directly and with the use of the graph theory alone.

Theorem 2. The number of labeled trees having n vertices partitioned in two sets A, B having respectively p and q vertices and in which the A point of label k has degree d_k and the B point of label k has degree δ_k is:

$$\tau = \frac{(p-1)!(q-1)!}{\prod_{k=1}^{p} (d_k - 1)! \prod_{k=1}^{q} (\delta_k - 1)!} \tag{32}$$

The demonstration of this theorem is given in the Appendix.

In the particular case we are interested in, the number of trees characterized by the vector $\mathbf{s}$ is:

$$\tau_s = \frac{(s_{\mathrm{A}} - 1)!(s_{\mathrm{B}} - 1)!}{\prod_{i=1}^{n} [(f_{\mathrm{A}_i} - 1)!]^{s_{\mathrm{A}^i}} \prod_{j=1}^{m} [(f_{\mathrm{B}_j} - 1)!]^{s_{\mathrm{B}^j}}} \tag{33}$$

$$\tau_s = (s_A - 1)!(s_B - 1)!\frac{\mathcal{P}}{\mathcal{J}} \tag{34}$$

Theorem 3. The number of graphs isomorphic to a given graph $\tau_s^{(i)}$ is defined by the relation:

$$\tau_s^{(i)} = \frac{\mathcal{S}}{|G_i|} \tag{35}$$

where $\mathcal{S} = \mathcal{S}_A\mathcal{S}_B$ with

$$\mathcal{S}_A = \prod_{i=1}^{n} s_{A_i}!$$

$$\mathcal{S}_B = \prod_{j=1}^{m} s_{B_j}!$$

The demonstration of this theorem is given in the Appendix.

For all of the isomers of the s graph, we have:

$$\tau_s = \sum_{i=1}^{I}\tau_s^{(i)} \tag{36}$$

$$\tau_s = \mathcal{S}\sum_{i=1}^{I}|G_i|^{-1} \tag{37}$$

By comparison with theorem 2, we obtain:

$$\sum_{i=1}^{I}|G_i|^{-1} = (s_A - 1)!(s_B - 1)!\frac{\mathcal{P}}{\mathcal{J}\mathcal{S}} \tag{38}$$

Theorem 4. Knowing $\sum_{i=1}^{I}|G_i|^{-1}$, we can determine the number of distinct ordered rooted trees $T_{s,A}$, $T_{s,B}$, and T_s:

$$T_{s,A} = T_{s,B} = a\frac{(s_A - 1)!(s_B - 1)!}{\mathcal{S}} \tag{39}$$

$$T_s = T_{s,A} + T_{s,B} \tag{40}$$

or

$$T_s = 2a\frac{(s_A - 1)!(s_B - 1)!}{\mathcal{S}} \tag{41}$$

From relations 41, 30, and 31, we can obtain directly the number of ordered trees rooted on any vertex and, in particular, the number of planted trees, which leads to the result obtained by Tutte,[17] using Lagrange's expansion.

Molecular Distribution

1. Determination of the Number of Node Rooted Ordered Trees. As in the case of order I systems,[13] the only trees having a chemical reality are the trees which are rooted on the nodes.

Consider an x-mer composed of x_A A monomers and x_B B monomers, characterized by type partitions given by the vectors $\mathbf{x}$, $\mathbf{x}_A$, and $\mathbf{x}_B$:

$$\mathbf{x} = [x_A, x_B] \qquad x = x_A + x_B \tag{42}$$

$$\mathbf{x}_A = [x_{A_1}, x_{A_2}, \ldots, x_{A_i}, \ldots, x_{A_n}] \qquad x_A = \sum_{i=1}^{n} x_{A_i} \tag{43}$$

$$\mathbf{x}_B = [x_{B_1}, x_{B_2}, \ldots, x_{B_j}, \ldots, x_{B_m}] \qquad x_B = \sum_{j=1}^{m} x_{B_j} \tag{44}$$

where x_{A_i} (x_{B_j}) is the number of monomers of type A_i (B_j) having the functionality f_{A_i} (f_{B_j}).

Assuming that different types of monomers have the same functionality, then they differ only by their chemical structure.

Associate to this x-mer an s-mer by the graphical procedure defined in the System Model section.

This s-mer tree has s vertices partitioned in the following: x node vertices characterized by the vectors $\mathbf{x}$, $\mathbf{x}_A$, and $\mathbf{x}_B$; and s_T terminal vertices characterized by the vector $\mathbf{s}_T$:

$$\mathbf{s}_T = [s_{TA}, s_{TB}] \qquad s_T = s_{TA} + s_{TB} \tag{45}$$

with

$$s_{TA} = \sum_{j=1}^{m} x_{B_j} f_{B_j} - x + 1 = x_B\bar{\varphi}_{xB} - x + 1 \tag{46}$$

$$s_{TB} = \sum_{i=1}^{n} x_{A_i} f_{A_i} - x + 1 = x_A\bar{\varphi}_{xA} - x + 1 \tag{47}$$

where $\bar{\varphi}_{xA}$ and $\bar{\varphi}_{xB}$ are respectively the number average functionalities of A monomers and B monomers constituting the x-mer

$$\bar{\varphi}_{xA} = \sum_{i=1}^{n} x_{A_i} f_{A_i}/x_A \tag{48}$$

$$\bar{\varphi}_{xB} = \sum_{j=1}^{m} x_{B_j} f_{B_j}/x_B \tag{49}$$

The conditions to have a tree are $s_{TA} \geq 0$ and $s_{TB} \geq 0$. Thus, for a given x_B, x_A must satisfy the relations:

$$x_A(\bar{\varphi}_{xA} - 1) \geq x_B - 1 \tag{50}$$

and

$$x_A \leq x_B(\bar{\varphi}_{xB} - 1) + 1 \tag{51}$$

The total number of vertices s of the s-mer is:

$$s = x + s_T \tag{52}$$

and the total number of edges a is:

$$a = x - 1 + s_T \tag{53}$$

or

$$a = x_A\bar{\varphi}_{xA} + x_B\bar{\varphi}_{xB} - x + 1 = x(\bar{\varphi}_x - 1) + 1 \tag{54}$$

where $\bar{\varphi}_x$ is the average functionality of all the monomers constituting the x-mer:

$$\bar{\varphi}_x = \frac{x_A\bar{\varphi}_{xA} + x_B\bar{\varphi}_{xB}}{x} \tag{55}$$

The numbers of ordered trees rooted on any A node ($T_{x,A}$), any B node ($T_{x,B}$), or any A or B node (T_x) are deduced from the number of ordered rooted trees $T_{s,A}$, $T_{s,B}$, or T_s defined by the vector $\mathbf{s}$ by using relations 30 and 31.

$$T_{x,A} = T_{s,A}\frac{x_A\bar{\varphi}_{xA}}{a} = T_s\frac{x_A\bar{\varphi}_{xA}}{2a} \tag{56}$$

$$T_{x,B} = T_{s,B}\frac{x_B\bar{\varphi}_{xB}}{a} = T_s\frac{x_B\bar{\varphi}_{xB}}{2a} \tag{57}$$

$$T_x = T_s\frac{(x_A\bar{\varphi}_{xA} + x_B\bar{\varphi}_{xB})}{2a} = T_s\frac{x\bar{\varphi}_x}{2a} \tag{58}$$

Theorem 4 gives

$$T_{s,A} = T_{s,B} = \frac{a(s_A - 1)!(s_B - 1)!}{\mathcal{S}} \tag{59}$$

and

$$T_s = \frac{2a(s_A - 1)!(s_B - 1)!}{\mathcal{S}} \tag{60}$$

where here

$$a = x(\bar{\varphi}_x - 1) + 1$$

$$s_A = x_B\bar{\varphi}_{xB} - x_B + 1$$

$$s_B = x_A\bar{\varphi}_{xA} - x_A + 1$$

$$\mathcal{S} = \mathcal{H}\mathcal{S}_T$$

and

$$\mathcal{H} = \mathcal{H}_{\mathrm{A}}\mathcal{H}_{\mathrm{B}}$$

$$\mathscr{S}_{\mathrm{T}} = s_{\mathrm{TA}}!s_{\mathrm{TB}}!$$

with

$$\mathcal{H}_{\mathrm{A}} = \prod_{i=1}^{n} x_{\mathrm{A}_i}!$$

$$\mathcal{H}_{\mathrm{B}} = \prod_{j=1}^{m} x_{\mathrm{B}_j}!$$

The numbers of node ordered trees rooted on any A node, any B node, or any A or B node are:

$$T_{x,\mathrm{A}} = \frac{x_{\mathrm{A}}\bar{\varphi}_{x\mathrm{A}}(s_{\mathrm{A}} - 1)!(s_{\mathrm{B}} - 1)!}{\mathscr{S}} \qquad (61)$$

$$T_{x,\mathrm{B}} = \frac{x_{\mathrm{B}}\bar{\varphi}_{x\mathrm{B}}(s_{\mathrm{A}} - 1)!(s_{\mathrm{B}} - 1)!}{\mathscr{S}} \qquad (62)$$

$$T_x = \frac{x\bar{\varphi}_x(s_{\mathrm{A}} - 1)!(s_{\mathrm{B}} - 1)!}{\mathscr{S}} \qquad (63)$$

In another way, expressions 61 to 63 may be written:

$$T_{x,\mathrm{A}} = \frac{x_{\mathrm{A}}\bar{\varphi}_{x\mathrm{A}}(x_{\mathrm{A}}\bar{\varphi}_{x\mathrm{A}} - x_{\mathrm{A}})!(x_{\mathrm{B}}\bar{\varphi}_{x\mathrm{B}} - x_{\mathrm{B}})!}{\prod_{i=1}^{n} x_{\mathrm{A}_i}!\prod_{j=1}^{m} x_{\mathrm{B}_j}!(x_{\mathrm{A}}\bar{\varphi}_{x\mathrm{A}} - x + 1)!(x_{\mathrm{B}}\bar{\varphi}_{x\mathrm{B}} - x + 1)!} \qquad (64)$$

$$T_{x,\mathrm{B}} = \frac{x_{\mathrm{B}}\bar{\varphi}_{x\mathrm{B}}(x_{\mathrm{A}}\bar{\varphi}_{x\mathrm{A}} - x_{\mathrm{A}})!(x_{\mathrm{B}}\bar{\varphi}_{x\mathrm{B}} - x_{\mathrm{B}})!}{\prod_{i=1}^{n} x_{\mathrm{A}_i}!\prod_{j:1}^{m} x_{\mathrm{B}_j}!(x_{\mathrm{A}}\bar{\varphi}_{x\mathrm{A}} - x + 1)!(x_{\mathrm{B}}\bar{\varphi}_{x\mathrm{B}} - x + 1)!} \qquad (65)$$

$$T_x = \frac{x\bar{\varphi}_x(x_{\mathrm{A}}\bar{\varphi}_{x\mathrm{A}} - x_{\mathrm{A}})!(x_{\mathrm{B}}\bar{\varphi}_{x\mathrm{B}} - x_{\mathrm{B}})!}{\prod_{i=1}^{n} x_{\mathrm{A}_i}!\prod_{j=1}^{m} x_{\mathrm{B}_j}!(x_{\mathrm{A}}\bar{\varphi}_{x\mathrm{A}} - x + 1)!(x_{\mathrm{B}}\bar{\varphi}_{x\mathrm{B}} - x + 1)!} \qquad (66)$$

Note the relations:

$$\frac{T_{x,\mathrm{A}}}{x_{\mathrm{A}}\bar{\varphi}_{x\mathrm{A}}} = \frac{T_{x,\mathrm{B}}}{x_{\mathrm{B}}\bar{\varphi}_{x\mathrm{B}}} = \frac{T_x}{x\bar{\varphi}_x} \qquad (67)$$

Equation 66 gives directly the number of all of the distinct molecules which may be built from x monomers.

2. Determination of the Probabilities $P_{x\mathrm{A}}$, $P_{x\mathrm{B}}$, and P_x of Finding Respectively an A Site, a B Site, and an A or B Site of x-Mer. By the same procedure as that described in our first paper,[13] we will determine the probability that an A site selected at random will be attached to an x-meric specific configuration (i.e., a node rooted ordered tree). This probability is the same for each x-meric specific configuration, whatever the kind of selected A site (i.e., type of monomer). This probability is given by:

$$\gamma_{x,\mathrm{A}} = \prod_{i=1}^{n}\rho_{\mathrm{A}_i}{}^{x_{\mathrm{A}^i}}\prod_{j=1}^{m}\rho_{\mathrm{B}_j}{}^{x_{\mathrm{B}^j}}p_{\mathrm{A}}{}^{x_{\mathrm{B}}}p_{\mathrm{B}}{}^{x_{\mathrm{B}}-1}(1 - p_{\mathrm{A}})^{x_{\mathrm{A}}\bar{\varphi}_{x\mathrm{A}}-x+1}(1 - p_{\mathrm{B}})^{x_{\mathrm{B}}\bar{\varphi}_{x\mathrm{B}}-x+1} \qquad (68)$$

We remark that in an ordered tree rooted on an A node, the number of reacted A sites is equal to the number of B nodes and the number of reacted B sites is equal to the number of A nodes less one. In the same way, we have for a B site:

$$\gamma_{x,\mathrm{B}} = \prod_{i=1}^{n}\rho_{\mathrm{A}_i}{}^{x_{\mathrm{A}^i}}\prod_{j=1}^{m}\rho_{\mathrm{B}_j}{}^{x_{\mathrm{B}^j}}p_{\mathrm{A}}{}^{x_{\mathrm{B}}-1}p_{\mathrm{B}}{}^{x_{\mathrm{A}}}(1 - p_{\mathrm{A}})^{x_{\mathrm{A}}\bar{\varphi}_{x\mathrm{A}}-x+1}(1 - p_{\mathrm{B}})^{x_{\mathrm{B}}\bar{\varphi}_{x\mathrm{B}}-x+1} \qquad (69)$$

Note the relation:

$$\gamma_{x,\mathrm{B}} = r\gamma_{x,\mathrm{A}} \qquad (70)$$

As $T_{x,\mathrm{A}}$ and $T_{x,\mathrm{B}}$ are respectively the number of ordered trees rooted on a node of type A and B, the probabilities $P_{x,\mathrm{A}}$ and $P_{x,\mathrm{B}}$ of finding respectively an A site and a B site in an x-mer are

$$P_{x,\mathrm{A}} = \gamma_{x,\mathrm{A}}T_{x,\mathrm{A}} \qquad (71)$$

$$P_{x,\mathrm{B}} = \gamma_{x,\mathrm{B}}T_{x,\mathrm{B}} \qquad (72)$$

Then the probability of finding an A or B site in an x-mer may be written:

$$P_x = \frac{r}{r + 1}\gamma_{x,\mathrm{A}}T_{x,\mathrm{A}} + \frac{1}{r + 1}\gamma_{x,\mathrm{B}}T_{x,\mathrm{B}} \qquad (73)$$

Using relation 70, we obtain:

$$P_x = \frac{r\gamma_{x,\mathrm{A}}}{r + 1}(T_{x,\mathrm{A}} + T_{x,\mathrm{B}}) = \gamma_x T_x \qquad (74)$$

since $T_x = T_{x,\mathrm{A}} + T_{x,\mathrm{B}}$ with

$$\gamma_x = \frac{r}{r + 1}\gamma_{x,\mathrm{A}} = \frac{1}{r + 1}\gamma_{x,\mathrm{B}} \qquad (75)$$

As in the preceding paper, we can easily calculate the fractions of all the reacted sites and all the unreacted sites A or B belonging to the x-mer.

3. Weight Distribution Functions $w_{x,\mathrm{A}}$, $w_{x,\mathrm{B}}$, w_x. When it is assumed that each monomer has the same weight, the weight distribution functions $w_{x,\mathrm{A}}$, $w_{x,\mathrm{B}}$, and w_x are respectively the fraction of initial A monomers, initial B monomers, and initial A or B monomers which belong to the x-mer.

If N_0 is the number of initial monomers partitioned in N_{A} A monomers and N_{B} B monomers, the number of A sites ($S_{x,\mathrm{A}}$), B sites ($S_{x,\mathrm{B}}$), and A or B sites (S_x) which belong to the x-mer is:

$$S_{x,\mathrm{A}} = w_{x,\mathrm{A}}N_{\mathrm{A}}\bar{\varphi}_{x\mathrm{A}} \qquad (76)$$

$$S_{x,\mathrm{B}} = w_{x,\mathrm{B}}N_{\mathrm{B}}\bar{\varphi}_{x\mathrm{B}} \qquad (77)$$

$$S_x = w_x N_0\bar{\varphi}_x \qquad (78)$$

with the relations

$$N_0 = N_{\mathrm{A}} + N_{\mathrm{B}} \qquad (79)$$

where

$$N_{\mathrm{A}} = AN$$

$$N_{\mathrm{B}} = BN$$

N being the Avogadro number.

$$\bar{\varphi}_x = \frac{w_{x,\mathrm{A}}N_{\mathrm{A}}\bar{\varphi}_{x\mathrm{A}} + w_{x,\mathrm{B}}N_{\mathrm{B}}\bar{\varphi}_{x\mathrm{B}}}{w_x N_0} \qquad (80)$$

The probabilities of finding an A site, a B site, and an A or B site of an x-mer are respectively the fraction of total A sites, total B sites, and total A and B sites belonging to an x-mer. The number of sites $S_{x,\mathrm{A}}$, $S_{x,\mathrm{B}}$, and S_x may also be written:

$$S_{x,\mathrm{A}} = P_{x,\mathrm{A}}N_{\mathrm{A}}\bar{\varphi}_{0\mathrm{A}} \qquad (81)$$

$$S_{x,\mathrm{B}} = P_{x,\mathrm{B}}N_{\mathrm{B}}\bar{\varphi}_{0\mathrm{B}} \qquad (82)$$

$$S_x = P_x N_0\bar{\varphi}_0 \qquad (83)$$

where $\bar{\varphi}_{0\mathrm{A}}$, $\bar{\varphi}_{0\mathrm{B}}$, and $\bar{\varphi}_0$ are respectively the number average functionalities of the A monomers, B monomers, and A and B monomers.

By comparison of relations 71, 72, and 75 with 81–83, we obtain the weight distribution functions $w_{x,\mathrm{A}}$, $w_{x,\mathrm{B}}$, and w_x:

$$w_{x,\mathrm{A}} = \frac{\bar{\varphi}_{0\mathrm{A}}}{\bar{\varphi}_{x\mathrm{A}}}P_{x,\mathrm{A}} = \frac{\bar{\varphi}_{0\mathrm{A}}}{\bar{\varphi}_{x\mathrm{A}}}\gamma_{x,\mathrm{A}}T_{x,\mathrm{A}} \tag{84}$$

$$w_{x,\mathrm{B}} = \frac{\bar{\varphi}_{0\mathrm{B}}}{\bar{\varphi}_{x\mathrm{B}}}P_{x\mathrm{B}} = \frac{\bar{\varphi}_{0\mathrm{B}}}{\bar{\varphi}_{x\mathrm{B}}}\gamma_{x,\mathrm{B}}T_{x,\mathrm{B}} \tag{85}$$

$$w_x = \frac{\bar{\varphi}_0}{\bar{\varphi}_x}P_x = \frac{\bar{\varphi}_0}{\bar{\varphi}_x}\gamma_x T_x \tag{86}$$

From expressions 84–86, by using relations 67 and 75, we obtain the relations:

$$\frac{w_x}{x\bar{\varphi}_0} = \frac{r}{r+1}\frac{w_{x,\mathrm{A}}}{x_\mathrm{A}\bar{\varphi}_{0\mathrm{A}}} = \frac{1}{r+1}\frac{w_{x,\mathrm{B}}}{x_\mathrm{B}\bar{\varphi}_{0\mathrm{B}}} \tag{87}$$

The weight distribution functions may be written:

$$w_x = \frac{xr\bar{\varphi}_0}{r+1}\bar{\omega}_{x,\mathrm{A}} \tag{88}$$

$$w_{x,\mathrm{A}} = x_\mathrm{A}\bar{\varphi}_{0\mathrm{A}}\bar{\omega}_{x,\mathrm{A}} \tag{89}$$

$$w_{x,\mathrm{B}} = x_\mathrm{B}\bar{\varphi}_{0\mathrm{B}}\bar{\omega}_{x,\mathrm{B}} \tag{90}$$

with

$$\bar{\omega}_{x,\mathrm{B}} = r\bar{\omega}_{x,\mathrm{A}} \tag{91}$$

and

$$\bar{\omega}_{x,\mathrm{A}} = \frac{\gamma_{x,\mathrm{A}}T_{x,\mathrm{A}}}{x_\mathrm{A}\bar{\varphi}_{x,\mathrm{A}}} \tag{92}$$

where

$$\bar{\omega}_{x,\mathrm{A}} = \frac{(x_\mathrm{A}\bar{\varphi}_{x\mathrm{A}} - x_\mathrm{A})!(x_\mathrm{B}\bar{\varphi}_{x\mathrm{B}} - x_\mathrm{B})!}{\prod_{i=1}^{n} x_{\mathrm{A}_i}!\prod_{j=1}^{m} x_{\mathrm{B}_j}!(x_\mathrm{A}\bar{\varphi}_{x,\mathrm{A}} - x + 1)!(x_\mathrm{B}\bar{\varphi}_{x,\mathrm{B}} - x + 1)!}\prod_{i=1}^{n}\rho_{\mathrm{A}_i}{}^{x_{\mathrm{A}i}} \times \prod_{j=1}^{m}\rho_{\mathrm{B}_j}{}^{x_{\mathrm{B}j}}p_\mathrm{A}{}^{x_\mathrm{B}}p_\mathrm{B}{}^{x_\mathrm{A}-1}(1 - p_\mathrm{A})^{x_\mathrm{A}\bar{\varphi}_{x\mathrm{A}}-x+1}(1 - p_\mathrm{B})^{x_\mathrm{B}\bar{\varphi}_{x\mathrm{B}}-x+1}$$

4. Number Distribution Function n_x. If N_x denotes the total number of x-mers, the number of sites S_x may be written in another way:

$$S_x = N_x\bar{\varphi}_x \tag{93}$$

By comparison of relations 93 and 83, we obtain:

$$N_x = \frac{\bar{\varphi}_0}{x\bar{\varphi}_x}P_x N_0 = \frac{r\bar{\varphi}_0}{r+1}\bar{\omega}_{x,\mathrm{A}}N_0 \tag{94}$$

We find, here again, the classical expression of Stockmayer.[7] If N is the number of molecules at p_A conversion, by definition, the number distribution function n_x may be written:

$$n_x = N_x/N \tag{95}$$

As the number average degree of polymerization, $\overline{\mathrm{DP}}_\mathrm{n}$, is

$$\overline{\mathrm{DP}}_\mathrm{n} = \frac{N_0}{N} = \frac{1}{1 - \frac{rp_\mathrm{A}}{r+1}\bar{\varphi}_0} \tag{96}$$

we obtain

$$n_x = \frac{r\bar{\varphi}_0\bar{\omega}_{x,\mathrm{A}}}{1 + r - rp_\mathrm{A}\bar{\varphi}_0} \tag{97}$$

Conclusion

As in the case of order I system copolycondensates, graph theory leads directly and readily to the very general form of the molecular distribution functions of order II system copolycondensates.

Appendix

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Theorem 2. The number of labeled trees with n vertices, partitioned in two sets A and B with respectively p and q elements and in which the ith vertex of A has degree d_i and the jth vertex of B has degree δ_j, for which the (A,B) partition realized a bicoloration, is:

$$\tau(n;d_1,\ldots,d_p;\delta_1,\ldots,\delta_q) = \frac{(p-1)!(q-1)!}{\prod_{i=1}^{p}(d_i - 1)!\prod_{j=1}^{q}(\delta_j - 1)!} \tag{32}$$

Proof. Let $\mathbf{T}(A,B;d_1,\ldots,d_p;\delta_1,\ldots,\delta_q)$ be the set of these trees with:

$$A = \{a_1,\ldots,a_p\} \qquad B = \{b_1,\ldots,b_q\}$$

if $T = (X,E)$ is one of these trees, we have:

$$X = A \cup B \qquad |X| = n = p + q \qquad |E| = p + q - 1$$

$$\sum_{i=1}^{p} d_i = \sum_{j=1}^{q}\delta_j = p + q - 1$$

$$\sum_{i=1}^{p}(d_i - 1) = (\sum_{i=1}^{p} d_i) - p = q - 1$$

$$\sum_{j=1}^{q}(\delta_j - 1) = (\sum_{j=1}^{q}\delta_j) - q = p - 1$$

Identity 32 is evident for $n = 2$ ($p = q = 1$, $d_1 = \delta_1 = 1$). Suppose that it is true up to $n - 1$ for any distribution of the degrees. We take $T \in \mathbf{T}(A,B;d_1\ldots d_p;\delta_1\ldots\delta_q)$. We can observe that

$$\tau(n;d_1\ldots,d_p;\delta_1,\ldots,\delta_q) = \tau(n;\delta_1,\ldots,\delta_q;d_1,\ldots,d_p)$$

and that one of the numbers d_i or δ_j is equal to 1. So that we can suppose that $d_1 = 1$. Then we remove from T the vertex a_1. We obtain a new tree with vertices $a_2,\ldots,a_p,b_1,\ldots,b_q$ and degrees $d_2,\ldots,d_p$, $\delta_1',\ldots,\delta_q'$ such that each δ_j' is equal to δ_j except for one equal to $\delta_j - 1$. Conversely, if at any tree of vertices $a_2,\ldots,a_p;b_1,\ldots,b_q$ of degrees $d_2,\ldots,d_p$; $\delta_1'',\ldots,\delta_q''$ such that each δ_j'' is equal to δ_j except $\delta_k'' = \delta_k - 1$ we add the vertex a_1 together with an edge $[a_1,b_k]$, we obtain exactly once only every tree belonging to $\mathbf{T}(A,B;d_1,\ldots,d_p;\delta_1,\ldots,\delta_q)$.

We obtain the recursive relation:

$$\tau(n;d_1,\ldots,d_p;\delta_1,\ldots,\delta_q) = \sum_{k=1}^{q}\tau(n-1;d_1,\ldots,d_p;\delta_1,\ldots,\delta_{k-1},\delta_k-1,\delta_{k+1},\ldots,\delta_q)$$

Then we have:

$$\tau(n;d_1,\ldots,d_p;\delta_1,\ldots,\delta_q) = \sum_{\substack{k=1\\ \delta_k>1}}^{q}\frac{(p-2)!(q-1)!}{[\prod_{i=1}^{p}(d_i - 1)!](\delta_1 - 1)!\ldots(\delta_k - 2)!\ldots(\delta_q - 1)!} = \frac{(p-2)!(q-1)!}{\prod_{i=1}^{p}(d_i - 1)!\prod_{j=1}^{q}(\delta_j - 1)!}\sum_{k=1}^{q}(\delta_k - 1)$$

$$\tau(n;d_1\ldots,d_p;\delta_1,\ldots,\delta_q) = \frac{(p-1)!(q-1)!}{\prod_{i=1}^{p}(d_i - 1)!\prod_{j=1}^{q}(\delta_j - 1)!}$$

Theorem 3. Let a given graph be characterized by the type partitions defined by the vectors $\mathbf{s}$, $\mathbf{s}_\mathrm{A}$, and $\mathbf{s}_\mathrm{B}$. The number $\tau_s^{(i)}$ of graphs isomorphic to that given graph is defined by the relation:

$$\tau_s^{(i)} = \frac{\prod_{i=1}^{n} s_{A_i}! \prod_{j=1}^{m} s_{B_j}!}{|G_i|} \qquad (35)$$

Proof. Let $G_i = (Y,F)$ be a tree representative of an isomer, whose vertex set Y is partitioned in colors and types by Y_{A_i} $(1 \leq i \leq n)$ and Y_{B_j} $(1 \leq j \leq m)$ with $|Y_{A_i}| = s_{A_i}$ and $|Y_{B_j}| = s_{B_j}$.

On the other hand, let X be a set of labels, itself partitioned in colors and types by X_{A_i} $(1 \leq i \leq n)$ and X_{B_j} $(1 \leq j \leq m)$, with $|X_{A_i}| = s_{A_i}$ and $|X_{B_j}| = s_{B_j}$. We want to count the labeled trees on X isomorphic to G_i.

All these graphs can be obtained from the bijections $\sigma X \rightarrow Y$ such that $[\forall x \in X_{A_i}\ (X_{B_j}) \sigma(x) \in Y_{A_i}\ (Y_{B_j})]$ by putting in G_i the vertex x in the place of $\sigma(x)$. We note $G_i(\sigma)$, the tree associated to σ in that way. The set S of these bijections has cardinality:

$$\mathcal{S} = \prod_{i=1}^{n} s_{A_i}! \prod_{j=1}^{m} s_{B_j}!$$

However, two of these bijections can define the same tree. We must study the equivalence relation R in S defined by $\sigma R \sigma'$ if and only if $G_i(\sigma) = G_i(\sigma')$. We prove the next property of relation R, $\sigma R \sigma'$, if and only if $\varphi = \sigma' \cdot \sigma^{-1}$ is an automorphism of G_i. First we suppost that $\sigma R \sigma'$ is true. Clearly the function $\varphi = \sigma' \cdot \sigma^{-1}$ is a bijection from G_i to G_i, and we know that $G_i(\sigma) = G_i(\sigma')$ and $\sigma' = \varphi\sigma$. Then, from the property for every x,x' belonging to X, $[\sigma(x),\sigma(x')] \in F$ if and only if $[\sigma'(x),\sigma'(x')] \in F$; it follows that for every y,y' belonging to Y, $[y,y'] \in F$ if and only if $[\varphi(y),\varphi(y')] \in F$. This means that φ preserves adjacency.

Finally φ preserves colors because if $y \in Y_{A_i}$ then $\sigma^{-1}(y) \in X_{A_i}$ and $\varphi(y) \in Y_{A_i}$ and if $y \in Y_{B_j}$ then $\sigma^{-1}(y) \in X_{B_j}$ and $\varphi(y) \in Y_{B_j}$. So that φ is indeed an automorphism of G_i.

Conversely, it is obvious that for any automorphism φ of G_i and any $\sigma \in S$, $\sigma' = \varphi\sigma$ is an element of S which verifies $\sigma R \sigma'$. To obtain $\tau^{(i)}$, we must then divide the number of bijections belonging to S by the number of elements of each equivalence class, namely the cardinality of the automorphism group of G_i.

$$\tau_s^{(i)} = \mathcal{S} / |G_i|$$

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Surface Modification of Fluorocarbon Polymers by Radiation-Induced Grafting for Adhesive Bonding

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ABSTRACT: The mutual irradiation of polymers in methyl acrylate (MA) vapor followed by hydrolysis treatment is a surface grafting technique which had been developed originally for surface modification of polyethylene (PE). The technique now has been successfully applied to surface modification of two radiation-degradative fluorocarbon polymers, poly(tetrafluoroethylene) (PTFE) and poly(chlorotrifluoroethylene) (PCTFE). The adhesive bond strengths reach a maximum value when the grafted surface is covered with an outer homopolymer layer consisting only of the monomer component. Although this relationship between bond strength and homopolymer surface coincides with that suggested in PE grafts, it is shown more clearly by ESCA analysis of the modified fluoropolymer surfaces. The thickness of the homopolymer layer passes through a maximum and then decreases with irradiation time or dose. This decrease may reflect the radiation degradation of fluoropolymer chains. The peel strengths of grafted PTFE sheets are much higher than those of sodium (Na)-etched PTFE sheets. This difference in bond improvement is discussed in terms of mechanical strength of the modified surface layers.

In order to obtain strong adhesive joints of inert fluorocarbon polymers, the surfaces must be modified before bonding. The most extensively investigated pretreatments involve Na-etched treatments, using Na–ammonia[1-3] and Na–naphthalene–tetrahydrofuran[4-7] complex solutions, and CASING[8,9] or glow discharge treatments.[10-13] Though work has been done on the adhesive properties of radiation-grafted PTFE,[14,15] no detailed studies have been published on the relationship between the bond strength and the surface structure. Mutual irradiation of PE in MA vapor and subsequent hydrolysis treatment have been found to yield a surface graft having high adhesive bondability to epoxy adhesives.[16,17] Since the radiation grafting of radiation-degradative fluorocarbon polymers such as PTFE and PCTFE requires a low radiation dose to prevent the degradation, it is interesting that this surface grafting

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