≥ 0.9), the agreement with $\overline{X}_1{}'_{max}$ is exact to three figures and the value for $\overline{X}_{1\,F_1=F_2}$ is close to $\overline{X}_{1\,max}$ and always between $\overline{X}_{1\,max}$ and $\overline{X}_1{}'_{max}$. Since this calculation requires no iterations, the necessary calculating power is reduced from a computer to a desk calculator.

Finally, it was stated that when the reactivity ratios are both between 0 and 1, an azeotrope would exist. In Figure 4 a plot of F_1 against f_1 shows this to be the case.

In summary, for a step copolymer system where structurally identical comonomer functional groups having different reactivities couple to form polymer, a block copolymer is predicted. Once the reactivity ratios of self-coupling to cross-coupling are determined, comonomer block lengths may be calculated and are found to increase with an increasing difference between the reactivity ratios. The calculation can be greatly simplified by assuming that the extent of conversion where the comonomers are entering the polymer at an equal rate corresponds to the point where a sufficient but not excessive quantity of the less reactive monomer has coupled to terminate the oligomeric blocks of the more reactive monomer.

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Number of Contacts between Distant Segments of a Polymer Chain. A Solution of the Problem of Self-Avoiding Random Walk

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ABSTRACT: A new algebraic method is proposed for the rigorous study of the self-avoiding random-walk problem. This method allows the separate calculation of the number of configurations of n segments with fixed values of the number of contacts between neighboring segments and between distant segments.

A flexible chain that can assume all possible positions on a lattice without intersection of segments (self-avoiding random walk) has been used for a long time as a model of polymers in highly dilute solutions.

The present paper reinvestigates this problem in order to explain the experimentally observed difference of solubility between random and sequential copolymers of equal quantitative and qualitative composition. It seems intuitively evident that this difference is due to the nature of contact between distant segments of the chain.

A first method, based substantially on the form of the configurations up to a length of chain $n = 11$, has given predictions in good qualitative agreement with experience for the thermodynamic properties of copolymers in solution.[1,2]

The author has then looked for an algebraic method to determine the number of configurations with x primary contacts between nearby segments of a chain (segments p and $p + 3$), u primary contacts between distant segments (segments p and $p + i$, with $i > 3$), and y secondary contacts between nearby segments (segments p and $p + 2$). This number is denoted by the symbol $[N]_n^{u,x,y}$.

The calculation is made for cubic lattices of two and three dimensions. A primary contact takes place if two segments of the chain are on sites whose distance is the lattice parameter; a secondary contact happens if they are on two sites whose distance is the diagonal of the lattice cell.

The main basic ideas of this method were described in a previous article.[3] Recall that the method consists of decomposing the configurations with $x \neq 0$ into subchains with $x = 0$ primary contacts between neighboring segments. We have then derived a recursion equation which determines the number of chains with $x = 0$ for any n. y is considered as a variable. The form of this equation allows the recursive calculation, on the one hand, of the number of configurations to eliminate because they would correspond to the crossing of a site already occupied by a chain (excluded volume) and, on the other hand, of the number of primary or secondary contacts between distant segments, from the knowledge of these values for the chains with $n - 1$ to y, $n - 1$ to $y - 1$, and $n - 2$ to $y - 1$ secondary contacts between neighboring segments on the chain. These values $[N]_n^{x=0,y}$ are used for the subchains that occur in the computation of the configurations with $x \neq 0$. These values are thus already corrected for the excluded volume corresponding to the crossing, by the subchain, of a site already occupied by one of its segments. The number of contacts between distant segments which this subchain has within itself is also known. There remains the evaluation of the volume excluded due to the crossing by a subchain of a site already occupied by a segment of another subchain and the calculation of primary contacts that different subchains can have with each other. The elimination of the configurations corresponding to this volume excluded and the calculation of the number of configurations having primary contacts are done by means of recursive equations.[3] We shall recall further the principle of this type of calculation. We have tried and we think we have succeeded in obtaining accurate values for the number of configurations, none being included more than once or being wrongly excluded.

The numerical results of our equations for a cubic planar lattice were compared with those obtained by Professor Durup[8] of Orsay by exact computer enumeration up to $n = 13$, thus a method quite different from ours. He especially counted contacts between distant segments. Our results are identical.

In the present paper, the algebraic calculation has been extended by deriving very easily programmable equations for large values of n. Numerical applications were made up to $n = 17$ with a pocket computer in order to compare our results with those of other authors.[4–7] These authors have treated the problem with a computer, and have obtained the total number of configurations for a given n. Their results are considered to be exact up to $n = 15$ (14 steps). By our method, this total number of configurations is obtained as a sum of a finite number of partial results which provide, in addition, the number of configurations with given characteristics. From $n = 3$ to 15, our results for this total number of configurations differ from those of the others by not more than ±0.0007%. The deviation is by no means systematic. For $n = 17$, the discrepancy is slightly larger, but we have reason to think that our result is more accurate. The advantage of the present algebraic method appears to be the absence of an increased discrepancy between our results and the (unknown) exact ones as computations for large numbers n are made. This is a consequence of the form of our equations.

The mechanism of derivation of configurations one from another which allows us to write these equations is indeed independant of n. Hence, we do think that our results which are accurate in the range of values where other methods give exact values (from $n = 3$ to 15) will remain accurate when the number of segments becomes large.

On the other hand, if one wants to know only the number of configurations of n segments with fixed values of x, y, and u, then this calculation can be done separately and directly. It is even possible to locate the x primary and y secondary nearby contacts at chosen sites.

I. Introductory Discussion

Before giving the equations found, let us recall briefly the principle of calculation for excluded volume and primary contacts between distant segments, done by means of recursive equations.[3] To understand this principle, we shall consider the simple example of configurations with $x = 0$, $u = 0$, $z = 4$, the number of which is given by:

$$[N]_n^{x=0,u=0,y} = [N]_{n-1}^{x=0,u=0,y} + [N]_{n-1}^{x=0,u=0,y-1} + [N]_{n-2}^{x=0,u=0,y-1} - C \quad (1)$$

This equation means that the number of configurations for the chain n with y secondary contacts between neighboring segments (SCN) is derived from the numbers of configurations of subchains $n - 1$ with y SCN and $y - 1$ SCN and of subchains $n - 2$ with $y - 1$ SCN.

If we introduce in eq 1 values of $[N]_{n-1}^{y}$, $[N]_{n-1}^{y-1}$ and $[N]_{n-2}^{y-1}$ corrected for the excluded volume and the primary contacts between distant segments (since we study the case $u = 0$), we shall obtain for $[N]_n^y$ a value corrected for configurations of type a and b but not of type c (Figure 1).

Indeed, the configuration a pertains to the group of subchains $n - 1$ with $y - 1$ SCN (the segment 1 of these subchains is the segment 2 of the chain n). The configuration b pertains to the group of subchains $n - 1$ with y SCN. The important point is that these two configurations have been eliminated when calculating the number of configurations of these subchains.

On the contrary, the configuration c, pertaining to the group of subchains $n - 1$ with y SCN, is not eliminated. Indeed, for such a subchain, there is no first neighbor contact between distant segments, since the first segment of this subchain is in 2, while, for the chain n, there appears a first neighbor contact between its segment 1 and another segment of the chain. Since we are interested here only with chains having $u = 0$, we have to exclude such configurations of the chain n having distant first-order contacts, produced by the passage

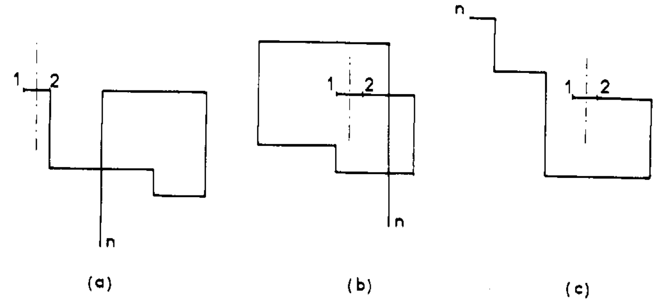
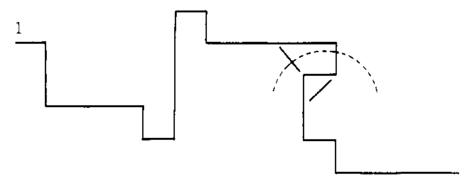


Figure 1.

of the chain on a site first neighbor of its segment 1. For this purpose, we introduce in (1) a corrective term C (substracted), which is specific of the length n



If now we calculate, for instance, $[N]_n^{x=0,u=1,y}$ (configurations having one distant first-order contact), the major part of the configurations is furnished by a recursive equation from the corrected values of $[N]_{n-1}^{x=0,u=1,y}$, $[N]_{n-1}^{x=0,u=1,y-1}$, and $[N]_{n-2}^{x=0,u=1,y-1}$, but, in this case, we must add a corrective term in order to take into account configurations of type c. This corrective term is still specific of the length n.

For the case $x \neq 0$, the basic recursive equations have the form:

$$[N]_n^{x,y} = [N]_{n_1}^{x-1,y_1(2)} \cdot [N]_{n-n_1}^{x=0,y-y_1(2)}$$

II. Configurations Corresponding to $1 < x < x_{max}$, $x = 1$, and $x = 0$

(A) $1 < x < x_{max}$ (n even: $x_{max} = (n-2)/2$; n odd: $x_{max} = (n-3)/2$). In the equations giving the number of these configurations there are only the symbols

$$[N]_n^y \quad \text{and} \quad [N]_n^{y(2)}$$

which represent the number of configurations of a chain of length n with $x = 0$ and $0 \leq y \leq n - 2$.

$$[N]_n^y = [N]_{n-1}^y + (z-3)[N]_{n-1}^{y-1} + [N]_{n-2}^{y-1} - [C]_n^y \text{ for } 1 < y \leq n-2 \quad (1')$$

z is the coordination number of the lattice. For $y = 0$, $[N]_n^0 = 1$ and $y = 1$, $[N]_n^1 = n - 2$

$$[N]_n^{y(2)} = (z-2)\{[N]_{n-1}^{y-1} - [N]_{n-2}^{y-2} + [N]_{n-3}^{y-3} - [N]_{n-4}^{y-4} + \ldots\} \pm (z-3) \quad (2)$$

Let us remember that the symbol $[N]_n^{y(2)}$ signifies that one of the second neighbor contacts of the chain occurs between segments 1 and 3 (or $n - 2$ and n). This is the case of the terminal subchains when we divide the chains with x first-neighbor contacts in $x + 1$ subchains (Figure 2).

In the same manner, the intermediary subchains have necessarily one of their second neighbor contacts between their segments 1 and 3 and another between their segments $n - 2$ and n (except for the intermediary subchains containing only 2 segments). To take account of these facts, we write that the subchains $n - 1$, $n - 2$, ... in the second member of eq 2 have a second neighbor contact between their segments $n - 2$ and n, or, which is the same for the number of configurations, between their segments 1 and 3.

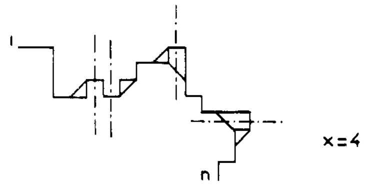


Figure 2.

$$[N]_n^{y(2),(n-1)} = (z-2)\{[N]_{n-1}^{y-1(2)} - [N]_{n-2}^{y-2(2)} + [N]_{n-3}^{y-3(2)} + \ldots\} \quad (3)$$

Considerations of the same nature allow us to write $[N]_n^{u\neq 0,x=0,y}$ in terms of $[N]_n^{u=0,x=0,y}$.

Because of the above, we can only see in the following equations symbols $[N]_n^y$ and $[N]_n^{y(2)}$. A practical consequence is that, if we want to know only the number of configurations of a chain of n segments, having x first-neighbor contacts between nearby segments of the chain and first-neighbor contacts between distant segments, the calculation can be made with the numerical values of:

$$[N]_{n-(2x+i)}^{y} \quad \text{and} \quad [N]_{n-(2x+i)}^{y(2)} \quad \text{with } i \geqslant 1$$

values given by recursive eq 1 and 2.

(a) *u* = 0.

$$[N]_n^{u=0,x,y} = z\{(y+1)[N]_{n-(2x+1)}^{y-1} + (y-1)[y(x-1)-1][N]_{n-(2x+1)}^{y-1(2)} + (x-2)(y-1)^2[N]_{n-(2x+1)}^{y-2(2)} + (x-3)(y-4)^2[N]_{n-(2x+1)}^{y-3(2)} + (x-4)(y-7)^2[N]_{n-(2x+1)}^{y-4(2)} + \ldots - C\} \quad (4)$$

(b) *u* = 1.

$$[N]_n^{u=1,x,y} = (z-3)\cdot a\cdot\{y[N]_{n-(2x+2)}^{y-2} + (y-1)[N]_{n-(2x+2)}^{y-2(2)} + (y-3)[N]_{n-(2x+3)}^{y-3(2)} + (y-5)[N]_{n-(2x+4)}^{y-4(2)} + \ldots\} + (z-3)\cdot C + (z-4)\{[N]_{n-(x+2)}^{y(2)} + 2(n-12)[[N]_{n-(x+3)}^{y-1(2)} + [N]_{n-(x+4)}^{y-1(2)} + \ldots + [N]_{y+1}^{y-1(2)}] - 2(n-10)[N]_{n-8}^{y-4(2)}\} \quad (5)$$

(c) *u* > 1. The number of configurations is obtained from the number of configurations for $u = 2$.

$$[N]_n^{u=2,x,y} = (z-3)\cdot a\cdot\{\alpha[N]_{n-(2x+2)}^{y-2} + \beta[N]_{n-(2x+2)}^{y-2(2)} + \gamma[N]_{n-(2x+3)}^{y-3(2)} + \delta[N]_{n-(2x+4)}^{y-4(2)} + \ldots - C\} + (z-3)D + (z-4)\{[N]_{n-(x+3)}^{y-1(2)} + 2(n-12)[[N]_{n-(x+4)}^{y-2(2)} + [N]_{n-(x+5)}^{y-2(2)} + [N]_{n-(x+6)}^{y-2(2)} + \ldots - 2(n-10)[N]_{n-9}^{y-4(2)}]\}$$
$$= (z-3)\cdot P + (z-3)D + (z-4)Q \quad (6)$$

Then, for $u > 2$:

$$[N]_n^{u,x,y} = (z-3)\cdot\{P - a\cdot(2u-5)[\alpha\{[N]_{n-(2x+3)}^{y-2} + [N]_{n-(2x+4)}^{y-4} + \ldots\} + \beta\{[N]_{n-(2x+3)}^{y-2(2)} + [N]_{n-(2x+4)}^{y-4(2)} + \ldots\} + C]\} + (z-4)\cdot\{[N]_{n-(x+u+1)}^{y-u+1(2)} + 2(n-12)[[N]_{n-(x+u+2)}^{y-u(2)} + \ldots + [N]_{y-u+2}^{y-u(2)}] + 2(n-10)[N]_{n-(u+7)}^{y-4(2)}\} \quad (7)$$

(i) The values of y in the preceding equations do not include the number of second-neighbor contacts situated inside the x first-neighbor contacts (their number is $2x$). (ii) The results of the equations have to be multipliated by: $A_4 = z(z-2)$ for the planar cubic lattice; $A_6 = z(z-2)(z-4)^{x-1}$ for the three-dimensional cubic lattice. $z(z-2)$ takes account of the lattice symmetries and $(z-4)^{x-1}$ of the different possible orientations of the x first-neighbor contacts on the lattice.

(B) x = 1. These configurations have no intermediary subchains, only terminal subchains, so their number is given by equations of a different form than those which correspond to $x > 1$.

(a) *u* = 0.

$$[N]_n^{u=0,x=1,y} = (z-3)[[(z-1)y + z + 1][N]_{n-3}^{y-1} - z[1+A][N]_{n-3}^{y-1(2)} - C] \quad (8)$$

(b) *u* = 1.

$$[N]_n^{u=1,x=1,y} = (z-3)[(y+3)[N]_{n-3}^{y-1(2)} + (y-3)[N]_{n-3}^{y-2(2)} - C] \quad (9)$$

(c) *u* > 1.

$$[N]_n^{u,x=1,y} = (z-3)[y\cdot[N]_{n-3}^{y-1(2)} - B[N]_{n-4}^{y-2(2)} - C\{[N]_{n-5}^{y-2(2)} + [N]_{n-6}^{y-2(2)} + \ldots\} + D] + (z-4)[y-A][n-(u+5)] \quad (10)$$

(C) x = 0. (a) *u* = 0.

$$[N]_n^{u=0,x=0,y} = [N]_n^y - (z-5)\sum_{u\geqslant 1}[Q]_n^{u,y} \quad (11)$$

$[N]_n^y$ is given by eq 1. For $[Q]_n^{u,y}$ see eq 12 and 13.

(b) *u* = 1.

$$[N]_n^{u=1,x=0,y} = [P]_n^{u=1,x=0,y} + (z-5)[Q]_n^{u=1,x=0,y} \quad (12)$$

(c) *u* > 1. For $u < u_L = n - 9$

$$[N]_n^{u,x=0,y} = [P]_n^{u,x=0,y} + (z-5)[Q]_n^{u,x=0,y}$$

$$[P]_n^{u,x=0,y} = [N]_{n-1}^{u,x=0,y} + (z-3)[N]_{n-1}^{u,x=0,y-1} + [N]_{n-2}^{u,x=0,y-1} + [C]_n^y \quad (13)$$

For $u = u_L = n - 9$

$$[N]_{n\ \text{pair}}^{u=n-9,x=0,y} = (z-3)[(y-4)(n-12) + (y-6)(n-14) + (y-8)(n-16) + \ldots] + (z-5)[Q]_n^{u=n-9,x=0,y}$$

$$[N]_{n\ \text{impair}}^{u=n-9,x=0,y} = (z-3)[(y-4)(n-11) + (y-6)(n-13) + (y-8)(n-15) + \ldots] + (z-5)[Q]_n^{u=n-9,x=0,y}$$

For $u > n - 9$

$$[N]_n^{u,x=0,y} = (z-5)[Q]_n^{u,x=0,y}$$

The explicit formulas for the terms A, B, C, D, Q appearing in the above equations depend slightly on the parity of n or x. If one is interested in rigorously exact values for the number of configurations, one has to take into account this parity effect. The corresponding equations for these various terms are given in Appendix I, while Appendix II gives an example of numerical calculations.

Appendix I

Equation 1. x cannot exceed a maximum value. For n even, $x_{\max} = (n-2)/2$, and for n odd, $x_{\max} = (n-3)/2$. y varies between 1 and $y_{\max}$. $y_{\max} = n - (3x+4)/2$ for x even, and $y_{\max} = n - 3(x+1)/2$ for x odd.

Expression of C: (i) n even: For $4 \leqslant y \leqslant n-5$

$$[C]_n^y = [C]_{n-1}^y + (z-3)[C]_{n-1}^{y-1} + [C]_{n-2}^{y-1} + (n-10)[N]_{n-8}^{y-4} + (n-11)[N]_{n-9}^{n-1,y-5} + (n-12)[N]_{n-10}^{y-6} + \ldots$$

For $y = 3$

$$[C]_n^3 = (z-3)\frac{n}{2}\frac{n-6}{4}$$

(ii) n odd: For $4 \leqslant y \leqslant n-5$

$$[C]_n^y = [C]_{n-1}^y + (z-3)[C]_{n-1}^{y-1} + [C]_{n-2}^{y-1} - \{[N]_{n-8}^{y-4} + (n-12)[N]_{n-9}^{y-5} + (n-13)[N]_{n-10}^{y-6} + \ldots\}$$

For $y = 3$

$$[C]_n^3 = (z-3)\frac{n-5}{2}\frac{n-7}{4}$$

Equation 4. For $y = 1$, one has $2(z-2)$ configurations. For $1 < y \leqslant y_{\max}$

Table I
Three-Dimensional Lattice [n = 15 (14 Steps)] (Total Number of Configurations: 4 468 955 764)

	x						
u	0	1	2	3	4	5	6
0	959 138 064	1 643 971 584	324 379 968	67 442 880	7 180 800	387 840	33 792
1	22 552 968	352 381 296	185 497 972	34 034 112	7 553 856	3 227 904	21 504
2	1 632 768	178 794 552	74 414 064	14 839 200	1 769 856	1 688 832	18 432
3	427 440	148 140 816	63 567 360	11 576 064	670 464	311 040	15 360
4	218 256	112 285 272	50 062 560	8 370 624	197 568	50 688	12 288
5	23 808	83 212 408	37 120 512	201 312	25 344	17 664	9 216
6	8 640	64 038 288	2 371 104	12 672	8 832	6 144	4 608
7	816	4 320	6 336	4 416	3 072	768	
8	192	1 344	2 208	1 536	384		
9	48	672	768	192			
10			96				
Total	984 003 000	2 587 830 552	737 422 948	136 483 008	17 410 176	5 690 880	115 200

Table II
Number of Configurations with x = 2: 15 362 978 × 24 × 2 = 737 422 948

	y								
u	1	2	3	4	5	6	7	8	9
0	8	150	3126	37 386	257 478	1 005 066	2 161 080	2 322 594	971 023
1	110	158	2280	19 833	120 426	481 573	1 150 456	1 412 916	676 725
2	2	104	276	4 077	35 950	169 826	441 759	586 728	298 449
3		2	198	2 057	22 990	125 631	363 918	521 193	288 331
4			62	765	10 914	75 912	265 977	432 945	256 395
5			8	420	2 020	29 137	171 608	344 132	226 019
6			6	207	1 784	7 521	16 270	16 899	6 708
7						2	38	38	54
8							2	36	48
9								2	14
10									2

$$C = (y-2)\left[n - \left(2y + \frac{x}{2} + 1\right)\right] - (y-4)[n - (2y + x - 1)]$$

for x pair and

$$C = (y-2)\left[n - \left(2y + \frac{x-1}{2} - 1\right)\right] - (y-4)[n - (2y + x - 1)]$$

for x impair.

Equation 5. For $y = 2$, one has 0 configurations, except for $n = 2x + 4$ which yields $2(z-3)$ configurations. For $2 < y < y_{\max}$: (α) x odd

$$a = 2(2y + 2x - 9)$$

$$\begin{aligned} C = \{&(y-3)[n-(y+2x-3)] \\ &+ (y-5)[n-(y+2x-2)] \\ &+ (y-7)[n-(y+2x-1)] + \ldots\}^{(x+1)/2} \\ &+ (x-2)\{(y-5)[n-(y+x)] \\ &+ (y-6)[n-(y+x+1)] + \ldots\} \\ &+ (x-4)\{(y-7)[n-(y+x+3)] \\ &+ (y-8)[n-(y+x+4)] + \ldots\} \\ &+ (x-6)\{\ldots \\ &\vdots \end{aligned}$$

(β) x even

$$a = 2y + 7\frac{x}{2} - 10$$

$$\begin{aligned} C = \Big\{&(y-2)\left[n - \left(y + 3\frac{x}{2}\right)\right] \\ &+ (y-3)\left[n - \left(y + 4\frac{x}{2}\right)\right] \\ &+ (y-4)\left[n - \left(y + 5\frac{x}{2}\right)\right] \\ &+ (y-5)\left[n - \left(y + 6\frac{x}{2}\right)\right] + \ldots\Big\}^{x/2} \\ &+ (x-3)\{(y-3)[n-(y+x+2)] \\ &+ (y-4)[n-(y+x+3)] + \ldots\} \\ &+ (x-5)\{(y-5)[n-(y+x+5)] \\ &+ (y-6)[n-(y+x+6)] + \ldots\} \\ &+ (x-7)\{(y-7)[n-(y+x+8)] \\ &+ (y-8)[n-(y+x+9) + \ldots\} \\ &+ \ldots \end{aligned}$$

For $y = y_{\max}$, $x > 2$, the number of configurations is given by C, with the exception of the term to the power $(\partial C + 1)/2$ and $\partial C/2$, respectively.

Equation 6. (α) x even.

$$a = y - 1,\ \alpha = y - 1,\ \beta = y - 2,\ \gamma = y - 4,\ \delta = y - 6, \ldots$$

$$\begin{aligned} C = (y-3)\{&[n-(2x+7)][N]_{n-(2x+4)}^{y-3(2)} \\ &+ [n-(2x+8)][N]_{n-(2x+5)}^{y-4(2)} + \ldots\} \\ &- (y-2)[n-(y+2x)] - (y-4)[n-(y+2x+2)] - \ldots \end{aligned}$$

$$D = \{(y-5)[n-(2y+x-7)] + (y-6)[n-(2y+x-6)] + \ldots\}^{x/2}$$
$$+ (x-2)\{(y-3)[n-(y+4)] + (y-5)[n-(y+7)] + (y-7)[n-(y+10)] + \ldots\}$$
$$+ (x-4)\{(y-5)[n-(y+6)] + (y-7)[n-(y+9)] + \ldots\}$$
$$+ (x-6)\{(y-7)[n-(y+8)] + \ldots\} + \ldots$$
$$\vdots$$

(β) x odd

$$a = 2(y-1), \alpha = y, \beta = y-1, \gamma = y-3, \delta = y-5, \ldots$$

$$C = (y-3)\{[n-(2x+6)][N]_{n-(2x+5)}^{y-3(2)} + [n-(2x+7)][N]_{n-(2x+6)}^{y-4(2)} + \ldots\}$$
$$- (y-4)[n-(y+x+2)] - (y-5)[n-(y+x+3)] - \ldots$$

$$D = \{(y-3)[n-(2y+x-4)] + (y-4)[n-2y+x-3] + \ldots\}^{(x+1)/2}$$
$$+ (x-2)\{(y-2)[n-(y+3)] + (y-4)[n-(y+6)] + \ldots\}$$
$$+ (x-4)\{(y-4)[n-(y+5)] + (y-6)[n-(y+8)] + \ldots\}$$
$$+ (x-6)\{(y-6)[n-(y+7)] + (y-8)[n-(y+10)] + \ldots\} + \ldots$$
$$\vdots$$

Equation 7 is valid for $2 < u < u_L$. For n even $u_L = n - (x + 6)$ and for n odd $u_L = n - (x + 7)$. For P see eq 6:

(i) x even

$$a = y-1, \alpha = y-2, \beta = y-3$$

$$C = (y-4)\{[n-(2x-2u+14)][N]_{n-(2x+6)}^{y-5} + [n-(2x-2u+15)][N]_{n-(2x+6)}^{y-5(2)}\}$$
$$+ (y-6)\{[n-(2x-2u+16)][N]_{n-(2x+8)}^{y-7} + [n-(2x-2u+17)][N]_{n-(2x+8)}^{y-7(2)}\}$$
$$+ (y-8)\{[n-(2x-2u+18)][N]_{n-(2x+10)}^{y-9} + [n-(2x-2u+19)][N]_{n-(2x+10)}^{y-9(2)}\}$$
$$+ \ldots$$
$$\vdots$$
$$+ (y-5)[n-(2y-2x-u+3)] + (y-6)[n-(2y-2x-u+4)] + \ldots$$

(ii) x odd

$$a = 2(y-2), \alpha = y-1, \beta = y-2$$

$$C = (y-3)\{[n-(2x-2u+11)][N]_{n-(2x+4)}^{y-4} + [n-(2x-2u+12)][N]_{n-(2x+4)}^{y-4(2)}\}$$
$$+ (y-5)\{[n-(2x-2u+13)][N]_{n-(2x+6)}^{y-6} + [n-(2x-2u+14)][N]_{n-(2x+5)}^{y-6(2)}\}$$
$$+ (y-7)\{[n-(2x-2u+15)][N]_{n-(2x+8)}^{y-8} + [n-(2x-2u+16)][N]_{n-(2x+8)}^{y-8(2)}\}$$
$$+ \ldots$$
$$\vdots$$
$$+ (y-4)[n-(2y-2x-u+3)] + (y-6)[n-(2y-2x-u+4)] + \ldots$$

When $u = u_L$

$$[N]_n^{uL,x,y} = (z-3)A + (z-4)Q \quad \text{for } 2 < y < y_{max} \qquad (7')$$

$$Q = [N]_{n-(x+u_L+1)}^{y-u_L+1} + 2(n-12)[[N]_{n-(x+u_L+2)}^{y-u_L(2)} + \ldots] + 2(n-10)[N]_{n-(u_L)}^{y-4(2)}$$

(α) x even

$$A = [(x-1) + \{n-(4x+5)\}][N]_{n-[5((x/2)-1)+u_L]}^{y-2(2)} - (y-4)[n-(2y-u_L+2)] - (y-5)[n-(2y-u_L+3)] - \ldots$$

(β) x odd

$$A = [x + \{n-(3x+3)\}][N]_{n-[5([(x+1)/2]-1)]+u_L-1]}^{y-2(2)} + (y-1)[n-(2y+u_L-6)] + (y-3)[n-(2y+u_L-5)] + \ldots$$

For $y = 2$ $[N]_n^{uL,x,z} = (z-4)Q$ (except for $u \leqslant x$; in this case, one has to add $2(z-3)$).

For $y = y_{max}$ $[N]_n^{uL,x,y_{max}} = (z-4)Q$.

For $u > u_L$, the number of configurations is $(z-4)Q$.

Number of Configurations for $x = x_{max}$. For n even

$$x_{max} = \frac{n-2}{2}, \quad u_{max} = n-8, \quad y_{max} = 0$$

For $u = 0$ there are $z - 3$ configurations and $y = 0$. For $1 \leqslant u \leqslant u_{max}$ there are $z - 4$ configurations and $y = 0$.

For n odd

$$x_{max} = \frac{n-3}{2}, \quad u_{max} = n-9, \quad 1 \leqslant y \leqslant 2$$

	$y =$	Configurations
$u = 0$	1	$2(z-2)$
	2	$2(z-3)(n-9)$
$1 \leqslant u \leqslant u_{max}$	1	$2(z-4)$
	2	$2(z-4)[n-(u+8)]$
$u = u_{max}$	1	$z-4$
	2	$2(z-4)[n-(n-1)]$

Equation 8. $1 \leqslant y \leqslant y_{max} = n - 4$ and $y = 1$ ($2(z - 4)$ configurations). For $y > 1$

(α) n even

$$A = \frac{n-12}{2}\frac{n-16}{2}$$

(β) n odd

$$A = \frac{n-11}{2}\frac{n-13}{2}$$

Expressions of C are: $y = 2$, $C = 0$; $y = 3$, $C = (z-2)(n-9)$; and $y > 3$, $C = (y+3)[N]_{n-5}^{y-2(2)}$.

Equation 9. For $y = 2$ there are $2(z - 2)$ configurations. For $2 < y \leqslant n - 4$ the expression of C is for $y = 3$

$$C = 2(n-7)$$

and for $y > 3$

$$C = (n-6)[n-(y+4)][1 + (n-14)\{[N]_{n-8}^{y-4(2)} + [N]_{n-10}^{y-4(2)} + [N]_{n-12}^{y-4(2)} + \ldots\} + (n-16)\{[N]_{n-10}^{y-6(2)} + \ldots\} + \ldots]$$

Equation 10. For $y = 2$ there are $2(z - 3)$ configurations and for $y = n - 4$ there are $2(z - 2)$ configurations. For $2 < y < n - 4$ and n odd $A = (n - 5)/2$ and for n even $A = (n - 4)/2$.

$$D = (y-2)[n-(2y-u+5)] + (y-4)[n-(2y-u+6)] + \ldots$$

For n even:

u even

$$\begin{cases} B_u = \dfrac{2n+7u-30}{2} + (z-4)a \\ C_u = \dfrac{n+u-13}{2} + (z-4)a \end{cases}$$

u odd

$$\begin{cases} B_u = \dfrac{2n + 7u - 33}{2} + (z - 4)a \\ C_u = \dfrac{3n + u - 32}{2} + (z - 4)a \end{cases}$$

$$a = 1 + \frac{n - 12}{4}\frac{n - 14}{2}$$

For n odd

u even > 2

$$\begin{cases} B_u = \dfrac{2n + 7u - 28}{2} + (z - 4)a \\ C_u = \dfrac{n + 2u - 12}{2} + (z - 4)a \end{cases}$$

u odd

$$\begin{cases} B_u = \dfrac{2n + 7u - 31}{2} + (z - 4)a \\ C_u = \dfrac{3n + u - 29}{2} + (z - 4)a \end{cases}$$

$$a = 1 + \frac{n - 11}{4}\frac{n - 13}{2} \qquad \text{for } B_2 \text{ only}$$

$$a = 1 + \frac{n - 13}{4}\frac{n - 15}{2} \qquad \text{for } u > 2$$

Equation 10 is valid for $1 < u < u_L$. For n even $u_L = n - 7$ and for n odd $u_L = n - 8$

$$[N]_n^{u_L,x=1,y} = (z - 3)[n - (2u_L - 2y + 7)] + (z - 4)[y - A][n - (u_L + 5)] \qquad (10')$$

This equation is valid for $4 \leqslant y < n - 6$. For $y = n - 6$, one has $2(z - 3) + (z - 4)[y - A][n - (u_L + 5)]$ configurations. When $u > u_L$, the number of configurations is given by the term $(z - 4)[y - A][n - (u + 5)]$ of eq 10′.

The results of the preceding equations must be multiplied by $z(z - 2)$ in order to account for the symmetries of the lattice. The same is true for the following special case $x = 0$.

Equation 12. (I)

$$[P]_n^{u=1,x=0,y} = [N]^u_{1,x=0,y,n-1} + (z - 3)[N]_{n-1}^{u=1,x=0,y-1} + [N]_{n-2}^{u=1,x=0,y-1} + [C]_n^{u=1,x=0,y}$$

$y \leqslant n - 5$. In order to start the recurrence, one has to calculate $[N]_n^{u=1,x=0,y=3}$ and $[N]_n^{u=1,x=0,y=4}$. For n even

$$[N]_n^{u=1,x=0,y=3} = (z - 3)\frac{n - 4}{2}\frac{n - 6}{2}$$

$$[N]_n^{u=1,x=0,y=4} = (z - 3)\left\{\frac{7}{2}\frac{n - 6}{2}\frac{n - 8}{2} + 5\frac{n - 8}{2}\frac{n - 10}{2} + 7\frac{n - 10}{2}\frac{n - 12}{2} + 9\frac{n - 12}{2}\frac{n - 14}{2} + \ldots\right\}$$

$$[C]_n^{u=1,x=0,y} = (n - 10)[N]_{n-7}^{y-4} + (n - 11)[N]_{n-8}^{y-4} + (n - 12)[N]_{n-9}^{y-4} + \ldots$$

For n odd

$$[N]_n^{u=1,x=0,y=3} = (z - 3)\frac{n - 5}{2}\frac{n - 7}{2}$$

$$[N]_n^{u=1,x=0,y=4} = (z - 3)\left\{2\frac{n - 5}{2}\frac{n - 7}{2} + 3\frac{n - 7}{2}\frac{n - 9}{2} + 4\frac{n - 9}{2}\frac{n - 11}{2} + \ldots\right\}$$

$$[C]_n^{u=1,x=0,y} = [N]_{n-7}^{y-4} + (n - 12)[N]_{n-9}^{y-4} + (n - 13)[N]_{n-11}^{y-4} + \ldots\}$$

(II)

$$[Q]_n^{u=1,x=0,y} = [N]_{n-1}^{u=1,x=0,y} + (z - 3)[N]_{n-1}^{u=1,x=0,y-1} + [N]_{n-2}^{u=1,x=0,y-2}$$

For $n = 6$, $y = 4$ there are $z - 4$ configurations.

Equation 13. For n even and u even

$$[N]_n^{u,x=0,y=4} = (z - 3)\left[[n - (3u + 2)] + \frac{[n - (2u + 4)]^2}{2} + \frac{[n - (3u + 4)]}{2}\frac{[n - (3u + 6)]}{2}\right]$$

$$[C]_n^y = (z - 3)[(y - 4)^2[n - (2y - u + 2)] + (y - 5)^2[n - (2y - u + 1)] + (y - 6)^2[n - (2y - u)] + \ldots]$$

For n even and u odd

$$[N]_n^{u,x=0,y=4} = (z - 3)\left[[n - (3u + 1)] + [n - (3u + 5)]^2 + \frac{[n - (2u + 4)]^2}{2}\right]$$

$$[C]_n^{n,y} = (z - 3)[(y - 3)(y - 4)^2[n - (2y - u + 3)] + (y - 4)(y - 5)^2[n - (2y - u + 1)] + (y - 5)(y - 6)^2[n - (2y - u - 1)] + \ldots]$$

For n odd and u even

$$[N]_n^{u,x=0,y=4} = (z - 3)\left[[n - (3u + 5)]^2 + [n - (3u + 3)] + \frac{[n - (2u + 3)][n - (2u + 5)]}{4}\right]$$

$$[C]_n^y = (z - 3)[(y - 4)^2[n - (2y - u + 1)] + (y - 6)^2[n - (2y - u)] + (y - 8)^2[n - (2y - u - 1)] + \ldots]$$

For n odd and u odd

$$[N]_n^{u,x=0,y=4} = (z - 3)\left[\frac{[n - (3u + 4)]}{2}\frac{[n - (3u + 6)]}{2} + 2[n - (3u + 2)] + \frac{[n - (2u + 1)]}{2}\frac{[n - (2u + 3)]}{2}\right]$$

$$[C]_n^y = (z - 3)[(y - 4)(y - 5)^2[n - (2y + u - 4)] + (y - 6)(y - 7)^2[n - (2y + u - 7)] + (y - 6)(y - 9)^2[n - (2y + u - 10)] + \ldots]$$

Appendix II

An Example of a Numerical Application. The calculation of the number of configurations for $n = 15$, $x = 2$, $u = 2$, $y = 5$.

Equation 6 gives

$$\begin{aligned}[N]_{15}^{2,2,5} = {} & 3 \times 4 \times [4[N]_9^3 + 3[N]_9^{3(2)} + 1[N]_8^{2(2)} + 3[15 - 9] \\ & + 1[15 - 11] - 2\{4[N]_7^{2(2)} + 3[N]_6^{1(2)} + 2[N]_5^{0(2)}] + 0 \\ & + 2[[N]_{10}^{4(2)} + 6[[N]_9^{3(2)} + [N]_8^{3(2)} + [N]_7^{3(2)} \\ & + [N]_6^{3(2)} + [N]_5^{3(2)}] - 10[N]_6^{1(2)}] \\ = {} & 12[4 \times 444 + 3 \times 201 + 19 + 22 - 130] \\ & + 2[1575 + 6 \times 445 - 10] \\ = {} & 27480 + 8470 = 35950\end{aligned}$$

$[N]_9^3$, $[N]_9^{3(2)}$, $[N]_8^{2(2)}$, etc., are yielded by eq 1 and 2.

For the numerical application, one has to remember that $[N]_n^y$ or $[N]_n^{y(2)}$ become 0 for $y > n - 2$. Much the same, the terms $n - i$, $y - i$, $z - i$ become 0 for $i > n$, $i > z$, and $i > y$.

References and Notes

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Synthesis and Properties of Aromatic and Extended Chain Polyamides

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ABSTRACT: Three areas of research on wholly aromatic polyamides are discussed. (1) Poly(1,3-phenyleneisophthalamide) was prepared in high molecular weight in chloroform or methylene chloride with tertiary amine acid acceptors. The degree of polymerization was enhanced by the presence of added or by-product tertiary amine salts. (2) 1,4-Aminobenzoyl chloride hydrochloride as crystalline needles was polymerized to high molecular weight in the solid state at high temperature and in suspension at low temperature in inert solvents with an acid acceptor. Both procedures led to the retention of the outward needle form. The polymer was crystalline and oriented crosswise of the needle structures. (3) A variety of extended chain polyamides, e.g., those based on such units as 1,4-phenylene, 2,6-naphthylene, *trans*-cyclohexylene, and *trans*-vinylene, were prepared which will form mesomorphic or liquid-crystalline solutions. These solutions depolarize transmitted, plane-polarized light and exhibit a reversal in viscosity–concentration relationship at the anisotropic–isotropic transition. Because these liquid-crystalline solutions contain microscopic domains of aligned and extended polymer chains, they yield molecularly oriented films and fibers upon extrusion. Such products have exceptionally high strength and modulus.

In a program of discovery in chemistry, success often seems to depend on a fortunate choice of ingredients, experimental conditions, and timing. Some call it serendipity. Described here are some key features of three pieces of research on aromatic polyamides, all of which involved in varying degrees some happy circumstances, a sharp eye, and often an element of care and persistence.

These three topics are: (1) preparation of polyamides in halogenated hydrocarbon–salt mixtures; (2) preparation of poly(1,4-benzamides) by thermal and suspension methods; and (3) extended chain polyamides and their liquid crystalline solutions.

Wholly aromatic polyamides in which the amide groups are linked directly to the rings have been known in the literature only for about 20 years when such a polymer was described in a patent to Magat.[3] An interfacial procedure was used and the molecular weight was not high by current standards.

At the time of our first programs on the synthesis of wholly aromatic polyamides there was a body of lore suggesting that, in addition to low reactivity, there were some peculiar side reactions which prevented formation of high polymers. Certainly, air oxidation of some diamines in the presence of alkali was a problem. Soon, as we developed low-temperature solution polycondensation methods,[4] the importance of monomer purity and polymer swelling and solubility were recognized.[5] At about the same time, modified interfacial procedures (that is, the use of water-miscible organic solvents) were found to yield high molecular weight aromatic polyamides.[6] Of the two methods, the solution method is more broadly applicable. These syntheses are most commonly carried out with diamines and diacid chlorides or amino-substituted acid chlorides.

Discussion and Results

For any of the low-temperature procedures there are a number of common controlling factors in their successful application. The principal ones are shown in Table I. To some degree an optimum condition in relation to one factor may make up for lack in another. For example, high reaction rate may compensate somewhat for low solubility. It is not the purpose here to examine these relations in detail, but the importance of some of them will become apparent in the discussion.

Preparation of Aromatic Polyamides in Halogenated Hydrocarbons. The first low-temperature solution preparations of polyamides from acid chlorides were carried out in halogenated hydrocarbons. Some of the first polymers were based on piperazines and aliphatic or aromatic diacids.[7,8] Tertiary amines were used as acid acceptors. Now it seems not to be generally known that this is a perfectly good route to many wholly aromatic polyamides. This is the first topic.

In a typical reaction, 1,3-phenylenediamine is allowed to react with isophthaloyl chloride in chloroform in the presence of triethylamine and added triethylamine hydrochloride (see Scheme I). Both the added and by-product triethylamine hydrochloride are soluble in the chloroform. The salt presumably forms a soluble complex with polymer, aiding solution and the polymerization process in a manner similar to that of LiCl in amide solvents. Viscous spinnable solutions can be formed as shown by the first set of data in Table II.

The polymerization series is arranged in order of decreasing salt concentration and polymer η_{inh}. Only at the highest concentration does the polymer remain dissolved. The first, second, and last polymerizations, wherein the salt to polymer mole ratio is about 4, show that dilution lowers the resulting degree of polymerization. The remaining three preparations show a decrease in viscosity of the polymer as the salt concentration decreases while polymer content is kept at about the same level. At low salt concentrations, high-speed stirring is needed in order to attain maximum mixing and uniform reaction before the polymer precipitates and further reaction essentially ceases.

If one adds anhydrous triethylamine hydrochloride to a