TABLE VIII
CLASSIFICATION OF CHARGE-TRANSFER POLYMERIZATIONS

K	Class	Examples[f]	Behavior
↓	A		No alternating copolymerization.
0.01	B		Alternating copolymerization in the presence of initiator.
		Cyclohexene–SO$_2$ (0.053, *n*-heptane, 25°)[a] PD–MAnh (0.055, CCl$_4$, 25°)	
↓	C	*cis*-2-Butene–SO$_2$ (0.076, *n*-heptane, 25°)[a] *trans*-2-Butene–SO$_2$ (0.082, *n*-heptane, 25°)[a]	Spontaneous alternating copolymerization near at room temperature. (The *K* value decreases with increasing solvent polarity.)
0.1		CEVE–MAnh (0.10, CCl$_4$, 30°) DME–MAnh (0.15, CCl$_4$, 25°)	
↓		1-Methylcyclopropene–SO$_2$[b]	
1.0			
↓		N-Vinylcarbazole-*p*-chloranil	(Spontaneous) ionic polymerization.
5.0	D	(3.2 ∼ 6.6, toluene ∼ acetonitrile)[c]	(The *K* value increases with increasing solvent polarity.)
↓		N-Vinylcarbazole–SO$_2$, X$_2$[d]	
∞	E	4-Vinylpyridine-*p*-chloranil (3:1 adduct)[e]	Formation of separable, stable complexes which cannot initiate.

[a] D. Booth, F. S. Dainton, and K. J. Ivin, *Trans. Faraday Soc.*, **55**, 1293 (1959). [b] S. Iwatsuki, *et al.*, *J. Polym. Sci.*, in press. [c] H. Nomori, M. Hatano, and S. Kambara, *ibid.*, *Part B*, **4**, 261 (1966). [d] K. Tsuji, K. Takakura, M. Nishii, K. Hayashi, and S. Okamura, *ibid.*, *Part A-1*, **4**, 2028 (1966). [e] H. Nomori, S. Ikeda, S. Kambara, and M. Hatano, 16th Symposium of the Polymer Society of Japan, Fukuoka, IB 05, 1967. [f] Inside the parentheses, equilibrium constant, solvent, and temperature are shown in that order.

of the van der Waals and the charge-transfer forces.[30] In cases of such systems having very small values of *K*, many problems remain to be solved.

Finally, according to our present knowledge it is possible to make a tentative classification of charge-transfer polymerizations as shown in Table VIII. By measuring the value of *K*, the mode of polymerization of the system can be predicted from such a classification, and *vice versa*.

As mentioned above, the complex mechanism theory can be explained without any apparent remarkable inconsistencies. Furthermore, products of the monomer (complex) reactivity ratios, r_1r_2, do not exceed unity as shown in Table V, and thus may suggest the usual free-radical copolymerization. But as to the mode of rearrangement of the complex to radicals, the question whether it is biradicals or monoradicals, and other many problems remain to be solved. These questions will be clarified eventually by investigations of the complex itself and of the polymerizations. We have obtained some kinetic data to obtain additional support for the complex mechanism theory and will report these results in another publication.

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(30) T. Matsuo and O. Higuchi, *Bull. Chem. Soc. Jap.*, **41**, 518 (1968).

The Efficiency of Phloroglucinol as a Trifunctional Branching Agent in Carbonate Copolymers

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ABSTRACT: Phloroglucinol is found to yield slightly less than three-fourths the maximum possible number of trifunctional branch points during the preparation of copolymers by solution condensations of bisphenol-A and phloroglucinol with phosgene in a methylene chloride–pyridine medium. This branching efficiency was determined by applying a recently developed correlation between the solution viscosities and weight-average molecular weights of randomly branched, polydisperse polymers to $[\eta]$ and $\bar{M}_w$ (by light scattering) data on six carbonate copolymers of phloroglucinol and bisphenol-A.

A method of evaluating the extent of branching in a polydisperse copolymer containing randomly distributed trifunctional branch points has been published recently.[1] The method was developed particularly for a copolymer formed by the random condensation of bifunctional and trifunctional reactants bearing functional group A with a bifunctional reactant bearing functional group B. This evaluation procedure is here applied to determine trifunctional branching

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(1) A. R. Shultz, *J. Polym. Sci.*, *Part A*, **3**, 4211 (1965).

TABLE I
PREPARATION OF CARBONATE COPOLYMERS OF PHLOROGLUCINOL AND BISPHENOL-A[a]

Sample	Phloroglucinol, g	Methylene dichloride, ml	Approximate[b] phosgene rate, g/min
A	0.070	360	0.60
B	0.140	360	0.60
C	0.420	460	0.60
D	0.420	485	0.60
E	0.420	470	0.65
F	2.52	700	0.60

[a] All preparations utilized 50.0 g of BPA and 41.7 g of pyridine. [b] The phosgene rate, although not absolute, was entirely reproducible.

in carbonate copolymers of phloroglucinol and bisphenol-A whose formations approximate most of the requirements of the theoretical model employed.

Experimental Section

The six polymers studied were prepared in essentially identical fashion. Only the quantities of phloroglucinol and of the diluent, methylene dichloride, were varied except for polymer E which was prepared at a slightly higher phosgenation rate. The preparations are summarized in Table I and a typical procedure is here detailed (polymer C).

Phosgene (Matheson) was bubbled, at a rate of approximately 0.60 g/min, through a rapidly stirred solution of 50.0 g (0.22 mol) of bisphenol-A (Dow), 0.420 g (3.3×10^{-3} mol) of phloroglucinol (Eastman), and 41.7 g (0.53 mol) of pyridine (Reilly) in 460 ml of methylene dichloride (Diamond). The reaction mixture was contained in a 1000-ml cylindrical glass resin flask equipped with a reflux condenser, thermometer, double-anchor glass stirrer and a gas addition tube extending to the bottom of the flask. Phosgene addition was terminated 5 min past the stoichiometric end point, which was recognized by a drop in reflux temperature in conjunction with an extreme increase in viscosity of the reaction mixture. The mixture was diluted with 300 ml of methylene dichloride and 50 ml of 13% hydrochloric acid was added slowly with stirring. The carbonate copolymer was precipitated by pouring the reaction mixture into 1500 ml of methanol in a rapidly moving Waring Blendor. The fibrous, white copolymer was filtered by suction and reslurried with 1000-ml portions of fresh methanol three additional times. After drying overnight at 85° (15 mm), the polymer had an intrinsic viscosity of 1.07 in 1,4-dioxane at 25.0°.

TABLE II
DATA AND DERIVED QUANTITIES FOR SIX TRIFUNCTIONALLY BRANCHED CARBONATE COPOLYMERS

Sample	Phloroglucinol, mol %	$10^{-3}\bar{M}_w$	$\langle[\eta]_{br}\rangle$	$\langle[\eta]_l\rangle$	$\langle[\eta]_{br}\rangle/\langle[\eta]_l\rangle$	γ	$10^3 N/X$	$10^3(N/X)_{feed}$	ϵ
A	0.25	76	0.93	1.00	0.93	0.255	0.76	1.25	0.61
B	0.50	71	0.82	0.955	0.86	0.44	1.88	2.5	0.75
C	1.50	280	1.07	2.36	0.45_5	0.905	5.77	7.6	0.76
D	1.50	54	0.61	0.795	0.76_5	0.62	5.12	7.6	0.67
E	1.50	78	0.70_5	1.015	0.695	0.715	5.45	7.6	0.72
F	8.4	86	0.39	1.085	0.36	0.945	33.9	45.9	0.74

Weight-average molecular weights of the carbonate copolymers were measured by light scattering in 1,4-dioxane at 25° using unpolarized 546-mμ light in a Brice-Phoenix series 1000 instrument. A refractive index increment,[2] dn/dc = 0.168 cm^3 g^{-1}, was measured and used, and an absolute turbidity of 1.16×10^{-3} cm^{-1} for "new" (post-1960) Cornell standard polystyrene (0.500 g/100 ml in toluene) was employed in calculations. Internal interference corrections (small in each case) were calculated on a random-coil basis using dissymmetry data obtained at 45 and 135° angles. Intrinsic viscosities were measured in 1,4-dioxane at 25.0° in calibrated Cannon-Ubbelohde dilution viscometers.

Results and Discussion

The experimental data and derived quantities for the six carbonate copolymer preparations studied are presented in Table II. The mole per cent of phloroglucinol in the feed (column 2) is equal to 100 (moles of phloroglucinol)/(moles of phloroglucinol + moles of bisphenol-A). Columns 3 and 4, respectively, give the measured weight-average molecular weights and intrinsic viscosities in 1,4-dioxane at 25.0°. The intrinsic viscosities, $\langle[\eta]_l\rangle$, listed in column 5 are calculated for polydisperse, linear polycarbonates of corresponding $\bar{M}_w$ using the relation[2]

$$\langle[\eta]_l\rangle = 6.0 \times 10^{-4}\bar{M}_w^{0.66} \qquad (1)$$

The branching efficiency of phloroglucinol in the copolymer is now obtained in the following manner. A branching index, γ, may be defined[1] for a polydisperse copolymer having randomly distributed trifunctional branch points by the relation

$$\gamma = {}^3/_4\bar{y}_w(N/X) \qquad (2)$$

where $\bar{y}_w$ is the weight-average degree of polymerization of the primary polymer distribution, *i.e.*, of the polymer which would exist under the same polycondensation conditions if all initial phloroglucinol OH groups were replaced by bisphenol-A OH groups, N is the number of trifunctional branch units (triply reacted phloroglucinol molecules in the present study), and X is the number of bifunctional, linear units (*vide post*) in the copolymer. The ratio of the intrinsic viscosities, $\langle[\eta]_{br}\rangle/\langle[\eta]_l\rangle$, of the branched copolymers and nonbranched polymers at the same weight-average degree of polymerization is a function of γ and a, where a is the exponent in the intrinsic viscosity–molecular weight relation for the linear, polydisperse polymer. For these polymers in dioxane at 25°, a = 0.66 (*cf.* eq 1). Figure 1 is a graphical representation[1] of $\langle[\eta]_{br}\rangle/\langle[\eta]_l\rangle$ as a function of γ for a = 0.66, assuming the Zimm–Kilb approximation $[\eta]_{br}/[\eta]_l = g^{1/2} = (\bar{R}_{br}^2/\bar{R}_l^2)^{1/2}$ for the individual polymer species.

Since $\bar{y}_w = (1 - \gamma)\bar{M}_w$/(gram molar chain unit weight), $\bar{M}_w$ and $\langle[\eta]_{br}\rangle/\langle[\eta]_l\rangle$ data allow calculation of N/X by means of Figure 1 and eq 2. The chain unit

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[2] P. L. Wineman, to be published.

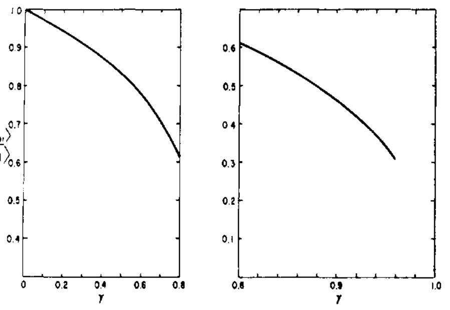
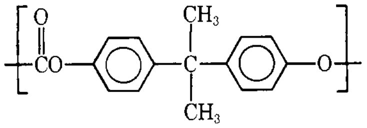


Figure 1. A plot of the intrinsic viscosity ratios, $\langle[\eta]_{br}\rangle/\langle[\eta]_l\rangle$, of polydisperse branched and linear polymers against branching indices, γ, in a solvent yielding a viscosity–molecular weight exponent of 0.66. The branched and linear polymers are of equal weight-average molecular weights.

of interest is that moiety associated with the splitting out of an HCl molecule in the condensation, *i.e.*, one-half of



and the gram molar chain unit weight is 127.14. Therefore, substitution for $\bar{y}_w$ and rearrangement of eq 2 yields

$$N/X = \frac{4}{3}\,\frac{127.14}{\bar{M}_w}\,\frac{\gamma}{1-\gamma} = 169.5\gamma/\bar{M}_w(1-\gamma) \qquad (2a)$$

From the polymerization feed composition is obtained

$$(N/X)_{feed} = (^1/_2)(\text{moles of phloroglucinol})/(\text{moles of bisphenol-A}) \qquad (3)$$

An efficiency of branching is then expressed by the ratio

$$\epsilon = (N/X)/(N/X)_{feed} \qquad (4)$$

Values of γ, N/X, $(N/X)_{feed}$, and ϵ obtained on the six carbonate copolymers in the manner just described are given in the last four columns of Table II. A reasonably constant value of ϵ, averaging 0.71, is found over the 37-fold range in feed ratios and over the observed range in γ from 0.255 to 0.945. The lowest value, $\epsilon = 0.61$, was obtained on the least-branched copolymer for which the sensitivity of the viscometric detection method is taxed. An average $\epsilon = 0.73 \pm 0.03$ is calculated from the data on samples B–F.

The relationships between functionality, degree of polymerization, extent of conversion and the critical conditions for gelation have been developed and summarized.[3,4] Application of these relationships has verified that relatively small amounts of polyfunctional reactants, in the usual polycondensation, will cause infinite network formation or gelation, at relatively low conversions.

Polycondensation *via* the phosgenation of diols, to form polycarbonates, markedly differs from conventional polyesterifications in two pertinent aspects.

a. Polycarbonate preparation, *via* phosgenation, usually entails addition of one of the difunctional reactants (phosgene) continuously during the course of polycondensation.

b. Polycondensation, *via* phosgenation, involves a two-step reaction, in which the second step, hydroxy–chloroformate condensation, is much slower than the first step, phosgene–hydroxyl condensation.[5]

$$\text{HOROH} + \text{COCl}_2 \xrightarrow{\text{base}} \text{HOROCOCl} + \text{base}\cdot\text{HCl}$$

$$\text{HOROCOCl} + \text{HOROH} \xrightarrow{\text{base}} \text{HOROCOOROH} + \text{base}\cdot\text{HCl}$$

It is therefore possible, by judicious control of the ratio of chloroformate to hydroxyl present in the reaction mixture when approaching the stoichiometric end point, to control the molecular weight of the polycarbonate obtained. This utilization of the classical "blocking effect"[6] results in essentially quantitative conversion, and affords a unique opportunity to circumvent the limitation, to relatively low degrees of branching, imposed by gelation in conventional polyesterifications.

There are many reaction variables, in the usual solution and emulsion phosgenations, that affect the ratio of chloroformate to hydroxyl present at the stoichiometric end point. The most significant of these are the rate of phosgene addition, the concentration of reactants, the stoichiometric excess of base, temperature, the efficiency of dispersion of phosgene in the reaction mixture, and the presence of additives such as water (which serve to reduce the stoichiometric excess of base in nonaqueous phosgenations) and monohydric phenols.

It is then possible, by trial and error, to arrive at a set of constant reaction conditions in which variation of only one factor permits essentially complete control of polymer molecular weight, and consequently avoidance of gelation. In the particular case of phosgenation of 2,2-bis(4-hydroxyphenyl)propane, BPA, *via* solution techniques, once a suitable reaction scheme has been obtained, it is most convenient to vary only the amount of inert diluent. Then at a constant level of branching agent used for copolymerization purposes, all other factors being equivalent, an increase in the quantity of diluent results in a lower molecular weight copolymer.

In assessing the applicability to this particular polycondensation of the theoretical model employed to measure branching, three factors might be mentioned. First, the theoretical molecular distribution function was derived on the basis of an extent-of-reaction-controlled primary chain length in a system containing equal numbers of the two types of reactive groups. The carbonate copolymers formed here had primary chain lengths ultimately controlled by the blocking effect of excess chloroformate end groups. This difference should not affect the form of the molecular weight distribution, but it would vitiate attempts to calculate

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(3) P. J. Flory, *J. Amer. Chem. Soc.*, **58**, 1877 (1936).

(4) W. H. Stockmayer, *J. Chem. Phys.*, **11**, 45 (1943); **12**, 125 (1944).

(5) H. Schnell, "Chemistry and Physics of Polycarbonates," Interscience Publishers, New York, N. Y., 1964, pp 10, 35.

(6) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 92, 93.

the primary chain lengths directly from the extent of reaction of –OH groups. Second, there is no measure here of the extent of ester interchange proceeding in the carbonate copolymers during condensation. Such interchange would be helpful in assuring the assumed random distribution of bonds throughout the polysperse copolymer. Lateral evidence (not presented) indicates essentially negligible ester interchange under the mild conditions employed in the present polycondensations. Finally, the finding of a branching efficiency less than unity suggests nonequivalence in the reactivities of the three phenolic –OH groups in phloroglucinol. Such nonequivalence should somewhat distort the branching complexity and thereby perturb the molecular distribution function. Such a perturbation is not even qualitatively estimated here, but it is believed not to have any appreciable influence on the above computation of branching efficiency.

The calculation of phloroglucinol's branching efficiency in phloroglucinol–bisphenol-A–phosgene condensations, by application of a theoretical treatment of intrinsic viscosity and weight-average molecular weight data, has led to self-consistent results. Although these results are not conclusive in themselves they are indicative of the utility and probable validity of the evaluation procedure.

Acknowledgment. The authors wish to thank Mr. Donald Papuga for assisting in the light scattering and solution viscosity measurements.

Molecular Weights of Homogeneous Samples of Deoxyribonucleic Acid Determined from Hydrodynamic Theories for the Wormlike Coil

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ABSTRACT: The molecular weights of a number of viral DNA's have been calculated using the hydrodynamic theories for the wormlike coil and the Flory–Mandelkern equation. The theoretical fit to the experimental sedimentation and viscosity data is good. The Kuhn statistical length of DNA has been calculated to be 805 Å in a solution with an ionic strength of 0.2. The ionic strength dependence of $1/\lambda$ is large and has been calculated. The range of molecular weights calculated for T-2 bacteriophage DNA is 94.4×10^6 to 105×10^6. The range calculated for T-7 bacteriophage DNA is 21.6×10^6 to 24.0×10^6.

Theoretical analysis of the hydrodynamic properties of dilute polymer solutions has been quite successful in the case of synthetic polymers. Flory[1] pointed out many years ago that the Kirkwood[2] theory for the translational friction factor for a random coil predicts a proportionality constant between $s_{20,w}$ and $M^{1/2}$ which is in precise agreement with experiment for polymers in θ solvents. Similarly, the Zimm[3] theory for the intrinsic viscosity of a random coil predicts a proportionality constant, ϕ, between $[\eta]$ and $M^{1/2}$ which is only 14% higher than that estimated by Flory[1] for a monodisperse polymer sample. This agreement is somewhat surprising in view of the assumptions which are required for the development of these theories. (1) The solvent is considered to be a hydrodynamic continuum. (2) The polymer chain is replaced by a string of beads which interact with each other as point disturbances. (3) The mathematical complexities of this problem have required the use of a premature average of the interaction tensor. (4) The intrinsic viscosity is calculated using a dynamic model (the Rouse chain) of balls connected by springs with average equilibrium lengths of zero. This model has $3N$ degrees of freedom where N is the number of beads in the chain, while any real chain would be expected to have only $2N + 1$ degrees of freedom.

Recognizing that the physical foundation for these theories is less than perfect, it remains true that their agreement with experiment has been impressive for ideal random coils. The extension of these theories to a molecular model which is reasonable for DNA (the wormlike coil) has been carried out in a series of papers,[4–8] using precisely the same assumptions which have been applied to the random coil. These newer papers provide results which apply to models with any properties intermediate between and including the properties of the rigid rod and the random coil. In addition, the effects of excluded volume have been treated.

Despite the good agreement between the theoretical proportionality constants and experiments, the Kirkwood–Riseman theory has frequently been considered incorrect because it predicts an intercept for the plot of $s_{20,w}$ *vs.* $M^{1/2}$ which is different from zero, while

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[1] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 14.

[2] J. G. Kirkwood, *J. Polym. Sci.*, **12**, 1 (1954).

[3] B. H. Zimm, *J. Chem. Phys.*, **24**, 269 (1956).

[4] J. E. Hearst and W. H. Stockmayer, *ibid.*, **37**, 1425 (1962)

[5] R. A. Harris and J. E. Hearst, *ibid.*, **44**, 2595 (1966).

[6] J. E. Hearst, R. A. Harris, and E. Beals, *ibid.*, **45**, 3106 (1966).

[7] H. B. Gray, Jr., V. A. Bloomfield, and J. E. Hearst, *ibid.*, **46**, 1493 (1967).

[8] J. E. Hearst, E. Beals, and R. A. Harris, *ibid.*, **48**, 5371 (1968).