In simulation studies, we now find that the presence of such structures in relatively small concentrations in softwood lignin is required if this lignin structure is to explain all experimental observations. These concern in particular the balance and distribution of hydroxyl groups (phenolic and primary and secondary aliphatic), the concentration of β–β, 5–5, and ether linkages, and the frequency of double bonds and external water additions to quinonemethide intermediates. Computer simulation techniques have again been found to provide a valuable aid to correlating structural details with a variety of analytical observations in lignin chemistry.

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(13) The higher yields from simulated oxidative degradations must be explained with the great instability of particularly benzene–dicarboxylic acids in the reaction medium.

A Method for Calculating Dihedral Angles in Helical Polymers with Given Values of Unit Height and Unit Rotation[1]

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Many homopolymers, sequential copolymers, and sometimes even random copolymers take helical conformations in solution and/or in crystal. In such fields as the x-ray crystrallography and the conformational energy analysis, oftentimes it becomes necessary to find a set of backbone dihedral angles $\omega_1, \omega_2, \ldots, \omega_m$ in a unit structure that generates a helical conformation with given values of unit height h and unit rotation ϕ. This paper describes a mathematical method to find such a set of dihedral angles. The case in which the value of the unit height h is not specified and only the value of the unit rotation ϕ is specified has been recently studied and solved by Yokouchi, Tadokoro, and Chatani.[3] The method in the present note is similar to the one developed previously[4] for finding a set of dihedral angles that generates conformations of cyclic chain molecules with C_n, I, or S_{2n} symmetry. Therefore we use some of the quantities and equations given in ref 4 without redefining them in the present paper.

The unit height h and the unit rotation ϕ are functions of the dihedral angles $\omega_1, \omega_2, \ldots, \omega_m$ in a unit structure, i.e.,

$$h = h(\omega_1, \omega_2, \ldots, \omega_m) \quad (1)$$

$$\phi = \phi(\omega_1, \omega_2, \ldots, \omega_m) \quad (2)$$

Our problem is to find sets of values of $\omega_1, \omega_2, \ldots, \omega_m$ for which the functions h and ϕ assume given values. In order to solve this problem we assume that the values of $\omega_1, \omega_2, \ldots, \omega_{m-2}$ are preassigned and regard eq 1 and 2 as algebraic equations for a pair of unknowns ω_{m-1} and ω_m. As before[4] we designate ω_{m-1} and ω_m by ξ and η in order to emphasize that they are unknowns.

In order to obtain the explicit forms of eq 1 and 2, a local coordinate system is defined corresponding to each of the variable backbone dihedral angles. Then, the mth coordinate system is related to the 0th one by the symmetry operation of helix. If we designate the matrix of rotation to bring the mth coordinate system into the same orientation as that of the 0th one by **U** and the position vector of the origin of the mth coordinate system with respect to the 0th one by **p**, the explicit forms of eq 1 and 2 are given by

$$\mathrm{Tr}\,\mathbf{U} = 2\cos\phi + 1 \quad (3)$$

$$\mathbf{u}\cdot\mathbf{p} = h \quad (4)$$

Here Tr means trace. The explicit forms of matrix **U** and vector **p** are given by eq I-7 and I-8 in terms of the backbone dihedral angles $\omega_1, \omega_2, \ldots, \omega_m$. The unit vector **u**, about which the rotation of the matrix **U** takes place, is given by eq I-34 in terms of elements of **U** and the angle of rotation ϕ. In some cases it is prefereable to use the following equation instead of eq 4.

$$\mathbf{p}\cdot\mathbf{U}\mathbf{p} = h^2(1-\cos\phi) + p^2\cos\phi \quad (5)$$

This equation can be derived from eq I-12 and 4. The matrix **U** and the vector **p** depend on the unknown backbone dihedral angles ξ and η in such a way that they can be expressed as **AXBY** and **a** + **AXb**, respectively, where **A** and **B** on one hand and **a** and **b** on the other hand are matrices and vectors, respectively, depending only on the known dihedral angles (i.e., $\omega_1, \omega_2, \ldots, \omega_{m-2}$), and **X** and **Y** are the matrices of rotation about the x axis by ξ and η, respectively. Explicit forms of these matrices and vectors are given in ref 4. If an additional matrix **C** is defined by **AXB** (eq I-36), eq 3 and 4 can now be written respectively as

$$\alpha\cos\eta + \beta\sin\eta + \gamma = 0 \quad (6)$$

and

$$\alpha'\cos\eta + \beta'\sin\eta + \gamma' = 0 \quad (7)$$

with

$$\begin{aligned} \alpha &= c_{22} + c_{33} \\ \beta &= c_{23} - c_{32} \\ \gamma &= c_{11} - 1 - 2\cos\phi \end{aligned} \quad (8)$$

and

$$\begin{aligned} \alpha' &= p_1(c_{23} - c_{32}) - p_2c_{13} + p_3c_{12} \\ \beta' &= -p_1(c_{22} + c_{33}) + p_2c_{12} + p_3c_{13} \\ \gamma' &= p_2c_{31} - p_3c_{21} + 2h\sin\phi \end{aligned} \quad (9)$$

where c_{ij} is the i,j element of matrix **C**, and p_i is the i component of vector **p**. In case eq 5 is used instead of eq 4, eq 5 can also be written as eq 7, but now with

$$\begin{aligned} \alpha' &= p_2(p_1c_{12} + p_2c_{22} + p_3c_{32}) + p_3(p_1c_{13} + p_2c_{23} + p_3c_{33}) \\ \beta' &= p_2(p_1c_{13} + p_2c_{23} + p_3c_{33}) - p_3(p_1c_{12} + p_2c_{22} + p_3c_{32}) \\ \gamma' &= p_1(p_1c_{11} + p_2c_{21} + p_3c_{31}) \\ &\quad - \cos\phi(p_1^2 + p_2^2 + p_3^2) - (1-\cos\phi)h^2 \end{aligned} \quad (10)$$

It is to be noted that c_{ij} and p_i are linear functions of cos ξ and sin ξ. Therefore, α, β, γ and α', β', γ' of eq 9 are linear and quadratic functions of cos ξ and sin ξ; α', β', γ' of eq 10 are polynomials of cos ξ and sin ξ of the third order. By solving eq 6 and 7 simultaneously, we have

$$\cos \eta = (\beta\gamma' - \gamma\beta')/(\alpha\beta' - \beta\alpha')$$
$$\sin \eta = (\gamma\alpha' - \alpha\gamma')/(\alpha\beta' - \beta\alpha') \qquad (11)$$

By squaring each of eq 11 and adding, we eliminate η and obtain an algebraic equation in a single unknown ξ.

$$(\beta\gamma' - \gamma\beta')^2 + (\gamma\alpha' - \alpha\gamma')^2 - (\alpha\beta' - \beta\alpha')^2 = 0 \qquad (12)$$

The left-hand side of this equation is a polynomial of cos ξ and sin ξ of the sixth (or, the 8th) order, when eq 9 (or, respectively, eq 10) is used for α', β', γ'. Real roots of this equation can easily be obtained numerically. If no helical structure with given values of unit height h and unit rotation ϕ is possible for the preassigned values of $\omega_1, \omega_2, \ldots, \omega_{m-2}$ and for any values of ω_{m-1} and ω_m (or ξ and η), then no real roots exist of eq 12. Once the value of ξ is determined by solving eq 12, the value of η can be determined by eq 11.

Special attention must be paid for the special cases of $\phi = 0$ and $\phi = \pi$. When $\phi = 0$, the polymer has the translational symmetry, and the matrix **U** becomes equal to the identity matrix **I**. This condition reduces the number of independent backbone dihedral angles by three. The additional condition that the unit height be equal to a given value h reduces the number by one more. In all, four backbone dihedral angles must be adjusted in order that a polymer has the translational symmetry with a given value of unit height h. This special case is excluded from the consideration in this paper of the general helical symmetries. When $\phi = \pi$, it is imperative to use eq 5 or 10 instead of eq 4 or 9. This is because the third term in the expression for γ' in eq 9 vanishes for $\phi = \pi$; thus, tailoring to the given height becomes impossible. We can avoid this difficulty by using eq 5 or 10.

References and Notes

(1) This work was supported by grants-in-aid from the Ministry of Education, Japan.

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Poly(2,4,7-trinitro-9-fluorenyl) Methacrylate. A New Electron Acceptor Polymer

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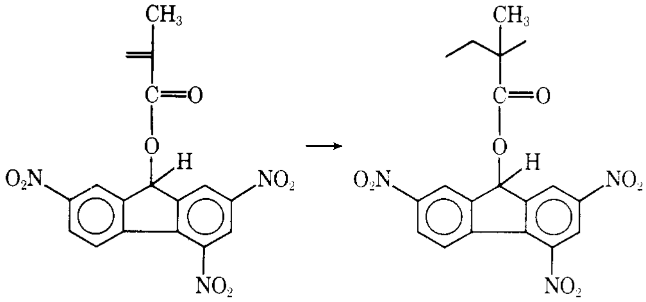
In contrast to the large number of electron donor type polymers that have been described in the literature, there have been very few reports of electron acceptor polymers. The ones that have been reported have, in the most part, dealt with the nitrated phenyl moiety[1-3] as the acceptor unit. Acceptor polymers based on polycyclic aromatic acceptors are rare indeed. A polyester based on the nitrated fluorenone nucleus has been reported by Sulzberg and Cotter[4] and Schulz and Tanaka[5] have reported polyesters based on the 9-spirocyclopropanetetranitrofluorene nucleus. This paper describes the preparation and some properties of an addition-type polycyclic aromatic acceptor polymer based on the trinitrofluorene nucleus poly(2,4,7-trinitro-9-fluorenyl) methacrylate (II).



I

II

(1)

Experimental Section

9-Diazo-2,4,7-trinitrofluorene (III). This compound was prepared according to the method by Colter and Wang[6] by first preparing 2,4,7-trinitrofluorenone hydrazone and then oxidizing to the diazo derivative with silver oxide in a yield of 75% (mp 214–215 °C) (lit.[6] mp 204–205 °C). The melting point was consistently higher than that reported over the course of several preparations.

2,4,7-Trinitro-9-fluorenyl Acetate (IV). This compound was prepared according to Colter and Wang[6] by refluxing 9-diazotrinitrofluorene in glacial acetic acid in a yield of 68% (mp 237–240 °C) (lit.[6] mp 240–242 °C).

2,4,7-Trinitro-9-fluorenyl Methacrylate (I). The diazotrinitrofluorene (10.0 g, 0.03 mol) was suspended in 150 ml of nitromethane and stirred with a magnetic stirrer. To this slurry 20 ml (0.22 mol) of freshly distilled methacrylic acid were added. Next, 4 ml of boron trifluoride etherate was added slowly via a syringe. Gas evolution was noted during addition. After stirring at room temperature for 1 h, a clear red solution resulted. The nitromethane was then removed on a rotary evaporator. When the pot material was reduced to an oil, the temperature was raised to 50 °C and the evaporation continued until an orange-yellow solid remained (approximately 1–2 h). Water (150 ml) was added to the flask and the contents were stirred at room temperature. After about an hour the suspension was filtered and then dissolved in 500 ml of benzene. This was heated to reflux and filtered hot to remove residual diazo compound. The benzene solution was evaporated on a rotary evaporator and the residual oil was allowed to solidify overnight. It was filtered, utilizing a minimum of ether, to effect the transfer. After drying at room temperature under vacuum for 24 h, 6.1 g (61%) of light orange powder (mp 148–150 °C) was obtained. The ir spectrum is shown in Figure 1a. NMR ($CDCl_3$) δ 2.0 (s, 3 H, CH_3), 5.65 and 6.15 (d, 2 H, $=CH_2$), 6.88 (s, 1 H, bridge H), 8.5 (m, 5 H, aromatic). Anal. Calcd for $C_{17}H_{12}N_3O_8$: C, 52.85; H, 3.11; N, 10.88. Found: C, 53.09; H, 2.91; N, 10.93.

Polymerization. A polymer tube was charged with 2.0 g of the monomer (I), 20 ml of reagent grade acetone, and 0.02 g (1 wt %) of AIBN. After three freeze–thaw cycles the tube was sealed under vacuum and placed into a 60 °C oil bath for 18 h. Precipitation into methanol yielded 1.5 g (75% conversion) of light yellow-orange powder which had an intrinsic viscosity at 30 °C in tetrahydrofuran of 0.128 dl g^{-1}. GPC analysis in tetrahydrofuran yielded $\bar{A}_n = 351$, $\bar{A}_w = 932$, MWD = 2.66. The ir spectrum is shown in Figure 1b. Anal. Calcd for $C_{17}H_{12}N_3O_8$: C, 52.85; H, 3.11; N, 10.88. Found: C, 52.85; H, 2.92; N, 11.07.

Uv Studies. Uv studies were done on a Cary Model 15 spectrophotometer utilizing fresh spectrograde tetrahydrofuran as solvent. All polymer solutions were run on the same day of preparation because of an apparent slow reaction of the solvent with the polymer leading to changes in the uv spectrum.

Results and Discussion

2,4,7-Trinitro-9-fluorenyl methacrylate (I) was prepared by the boron trifluoride etherate catalyzed reaction of 9-diazo-2,4,7-trinitrofluorene (III) with methacrylic acid in nitromethane (eq 2). Direct addition of methacrylic acid to III, as found by Colter and Wang[6] for acetic acid addition and described for the reaction of 9-anthryldiazomethane with acrylic acid,[7] was not possible since the methacrylic acid polymerized under the reaction conditions. Other attempts at preparing I through a solvolysis type reaction of 2,4,7-trinitro-9-fluorenyl tosylate and via the addition of methacryloyl chloride to 2,4,7-trinitro-9-fluorenol were all unsuccessful. The successful conditions, using a Lewis acid catalyst, were origi-