(224–226 °C) and by infrared spectral comparison with an authentic sample. To the reaction mixture was then added 1,7-dichlorooctamethyltetrasiloxane (10.5 g, 0.030 mol) and the reaction mixture was stirred for 3 h. ^{31}P NMR analysis showed that **15** had formed and had a spectrum identical with that of **5b**. The reaction mixture was filtered under nitrogen, the dioxane was removed under reduced pressure, and dry hexane was added. The resultant solution was then cooled to 0 °C and was filtered under nitrogen to remove $Ph_3SiOSiPh_3$. The filtrate was evaporated to dryness under reduced pressure and the residue was vacuum distilled (160–180 °C/0.05 mmHg) to yield species **15**, identified by gas chromatography/mass spectrometry techniques.

Formation of $(NPCl_2)_n$ from $(NPCl_2)_3$ in $(OSiMe_2)_3$. In a typical experiment $(NPCl_2)_3$ (7.00 g, 0.0202 mol) and $(OSiMe_2)_3$ (4.50 g, 0.0202 mol) were heated together at 250 °C until the solution became slightly viscous ($\simeq$24 h) but remained clear. The tube was cooled to room temperature and was opened in a nitrogen-filled glovebag. The contents were transferred to a vacuum sublimator and heated at 80 °C until all the volatile species had been removed. The white polymeric residue was identified as $(NPCl_2)_n$ by ^{31}P NMR spectroscopy (singlet at −18.8 ppm). The polymer was purified for elemental analysis by precipitation 3 times from dry THF into dry hexane in a nitrogen-filled glovebag. The yield of the unpurified polymer was typically 1.8 g (26%), based on the amount of $(NPCl_2)_3$ recovered.

Reactions of $(NPCl_2)_3$ with $(OSiMe_2)_4$ or $(Me_3Si)_2O$. The reaction times at 250 °C ranged from 21 to 158 h, with ratios of $(NPCl_2)_3$ to $(OSiMe_2)_4$ being varied from 1.5:1 to 36:1, and of $(NPCl_2)_3$ to $(Me_3Si)_2O$ from 1:1 to 10:1.

Acknowledgment. We thank the National Science Foundation Polymers Program and the U.S. Army Research Office for the support of this work. We also acknowledge the technical assistance provided by M. S. Connolly, J. L. Desorcie, and K. D. Lavin.

Registry No. 1, 940-71-6; 3, 541-05-9; 4, 556-67-2; $(Me_3Si)_2O$, 107-46-0.

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Thermodynamics of Polymerization for *cis*- and *trans*-Polyalkenamers and Its Application to the Polymerization of Cyclopentene

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ABSTRACT: *cis*- and *trans*-polyalkenamers may be obtained from equilibrium polymerizations of a certain number of monomers. The thermodynamics of these polymerizations is reexamined by taking into account the fact that the polymer is made of two types of distinguishable monomer units. A free energy term for the distribution of the cis and trans units in the polyalkenamer is added to the free energy for the conversion of pure monomer into pure amorphous *cis*- and *trans*-polyalkenamers. From the derived equation it is found that, for a given temperature, the proportion of cis and trans units in the polymer ought to be unique and independent of the solvent used when the configuration of the polyalkenamer is thermodynamically controlled. The equilibrium monomer concentration depends on the solvent and the configuration of the polymer formed. The equations are applied to the equilibrium polymerization of cyclopentene into polypentenamer at various temperatures with various catalysts. Computed values are in good agreement with reported experimental values.

Polymerization of dienes and cycloalkenes usually leads to the formation of linear unsaturated polymers (polyalkenamers) having one double bond per monomer unit. Depending on the catalysts used the configuration of the double bonds would be predominantly cis or trans. In the case of cycloalkenes, an equilibrium between monomer and active polymer can be reached in a certain number of polymerizations.[1-3] Since the free energy of polymerization

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is different for the *cis-* and *trans-*polyalkenamers, the equilibrium monomer concentration will vary according to whether a *cis-* or *trans-*polyalkenamer is formed. If the catalyst is stereospecific, the polyalkenamer will be 100% cis or trans. The problem then can be solved in a straightforward manner through the equation[4,5]

$$\Delta G_{\mathrm{lc}} = RT[\ln \phi_{\mathrm{m}} + 1 + \phi_{\mathrm{s}}(\chi_{\mathrm{ms}} - \chi_{\mathrm{sp}}(\bar{V}_{\mathrm{m}}/\bar{V}_{\mathrm{s}})) + \chi_{\mathrm{mp}}(\phi_{\mathrm{p}} - \phi_{\mathrm{m}})] \tag{1}$$

where ϕ_{m}, ϕ_{s}, and ϕ_{p} represent the volume fraction of monomer, solvent, and polymer, respectively, under equilibrium conditions. χ is the Flory–Huggins interaction parameter between the two components indicated by the subscripts. ΔG_{lc} is the free energy change for the conversion of 1 mol of pure monomer into pure amorphous polymer of infinite molecular weight with a given configuration. $\bar{V}_{\mathrm{m}}$ and $\bar{V}_{\mathrm{s}}$ are the molar volumes of monomer and solvent, respectively; R is the gas constant and T is the temperature. If the catalyst is not stereospecific, various proportions of cis and trans double bonds will form under equilibrium conditions, the proportiona of which are determined by the thermodynamics of the polymerization. Then the value of ΔG_{lc} varies with the cis and trans proportions and hence the equilibrium monomer concentration. However, since two types of structural units are formed under equilibrium conditions, the situation is more complicated than described by eq 1 and the thermodynamics needs to be reexamined accordingly. In addition to the monomer–polymer equilibrium, a ring–chain equilibrium also takes place. However, because the volume fraction of the cyclic species is of the order of 0.01,[6] the effect of that equilibrium on the monomer–polymer equilibrium is negligible.

A General Approach

A simple approach to equilibrium polymerization involving the formation of polyalkenamers is to set the free energy change for the polymerization of 1 mol of monomer as

$$\Delta G_{\mathrm{lc}} = x_{\mathrm{cis}}\Delta G_{\mathrm{cis}} + x_{\mathrm{trans}}\Delta G_{\mathrm{trans}} \tag{2}$$

and substituting in the left-hand side of eq 1. In this equation ΔG_{cis} and $\Delta G_{\mathrm{trans}}$ are the free energy change for the conversion of 1 mol of pure liquid monomer into 1 mol of monomer unit (1 base-mol) of amorphous *cis-* and *trans-*polyalkenamer, respectively. x_{cis} and x_{trans} are the mole fraction of cis and trans units in the polymer formed at equilibrium, bearing in mind that

$$x_{\mathrm{cis}} + x_{\mathrm{trans}} = 1 \tag{3}$$

Substitution of eq 2 into eq 1 would imply a simple additivity of the thermodynamic parameters upon the formation of two different types of monomer units. This approach does not take into account that an entropy term ought to be used due to the fact that two distinguishable monomer units can be found in the same polymer. This entropy term has to be added to the entropy change for the conversion of monomers into polymers of a given configuration.

The situation encountered in the formation of polyalkenamer with monomer units of two configurations resembles that in both homo- and copolymerization. It is similar to homopolymerization with respect to the formation of atactic polymer from a single monomer, and to copolymerization with respect to the formation of a polymer containing two types of monomer units. The latter aspect can be used in order to determine the additional entropy term. The starting point is a variant of the model used in the treatment of equilibrium copolymerization in solution.[7] In reference to this model, eq 2 is rewritten as

$$\Delta G_{\mathrm{lc}} = x_{\mathrm{cis}}\Delta G_{\mathrm{cis}} + x_{\mathrm{trans}}\Delta G_{\mathrm{trans}} + \Delta G_{\mathrm{D}} \tag{4}$$

where ΔG_{D} is the contribution to ΔG_{lc} arising from the fact that two types of monomer units are distributed in the polymer. This term is different from ΔG_{D} found in copolymerization where it refers to the distribution of four interunit bonds (A–A, A–B, B–B, B–A). In polyalkenamers the interunit bonds are identical and the difference between the monomer units comes solely from the configurations of the double bond within the unit. ΔH_{D}, the enthalpy change associated with this process, is nil so that

$$\Delta G_{\mathrm{D}} = -T\Delta S_{\mathrm{D}} = -kT \ln \Omega \tag{5}$$

where k is the Boltzmann constant and Ω represents the number of ways of arranging a total of N (the Avogadro number) monomer units consisting of N_{cis} and N_{trans}, the number of cis and trans monomer units, respectively. Using the law of permutation, one obtains

$$\Delta S_{\mathrm{D}} = k \ln \Omega = k \ln (N!/N_{\mathrm{cis}}!N_{\mathrm{trans}}!) \tag{6}$$

When Stirling's approximation is used, and with $N_{\mathrm{cis}} = x_{\mathrm{cis}}N$ and $N_{\mathrm{trans}} = x_{\mathrm{trans}}N$, eq 6 becomes

$$\Delta S_{\mathrm{D}} = -Nk(x_{\mathrm{cis}} \ln x_{\mathrm{cis}} + x_{\mathrm{trans}} \ln x_{\mathrm{trans}}) \tag{7}$$

With substitution of eq 5 and 7, eq 4 becomes

$$\Delta G_{\mathrm{lc}} = x_{\mathrm{cis}}\Delta G_{\mathrm{cis}} + x_{\mathrm{trans}}\Delta G_{\mathrm{trans}} + RT(x_{\mathrm{cis}} \ln x_{\mathrm{cis}} + x_{\mathrm{trans}} \ln x_{\mathrm{trans}}) \tag{8}$$

Polymerization in Solution

In order to obtain an expression in terms of the variables measured under equilibrium conditions, using the approach for equilibrium copolymerization[7] one can write

$$x_{\mathrm{cis}} = K \exp(-\Delta G_{\mathrm{cis\text{-}ss}}/RT) \equiv K \exp(X) \tag{9}$$

$$x_{\mathrm{trans}} = K \exp(-\Delta G_{\mathrm{trans\text{-}ss}}/RT) \equiv K \exp(Y) \tag{10}$$

where K is a constant. $\Delta G_{\mathrm{cis\text{-}ss}}$ and $\Delta G_{\mathrm{trans\text{-}ss}}$ represent the free energy change for the conversion of 1 mol of monomer to polymer, the process taking place in solution. The general expression for the free energy of polymerization in solution is[5]

$$\Delta G_{\mathrm{ss}} = -\overline{\Delta G}_{\mathrm{m}} + \Delta G_{\mathrm{lc}} + \overline{\Delta G}_{\mathrm{p}} \tag{11}$$

which becomes under equilibrium conditions

$$\Delta G_{\mathrm{lc}} = \overline{\Delta G}_{\mathrm{m}} - \overline{\Delta G}_{\mathrm{p}} \tag{12}$$

where $\overline{\Delta G}_{\mathrm{m}}$ is the partial molar free energy of the monomer in the equilibrium mixture relative to that of the pure liquid monomer, and $\overline{\Delta G}_{\mathrm{p}}$ is the partial molar free energy of the polymer (per base-mole) in the equilibrium mixture relative to that of the pure amorphous polymer. It is worth mentioning that whereas $\Delta G_{\mathrm{ss}} = 0$ for the overall reaction, no assumption is made as far as $\Delta G_{\mathrm{cis\text{-}ss}}$ and $\Delta G_{\mathrm{trans\text{-}ss}}$ are concerned. Substituting eq 9, 10, and 12 into eq 8, one obtains

$$-\overline{\Delta G}_{\mathrm{m}} + \overline{\Delta G}_{\mathrm{p}} + \Delta G_{\mathrm{cis}}K \exp(X) + \Delta G_{\mathrm{trans}}K \exp(Y) + RT[K \exp(X)(X + \ln K) + K \exp(Y)(Y + \ln K)] = 0 \tag{13}$$

Using the definitions of eq 9, 10, and 3, eq 13 is reduced to

$$RT \ln K = 0 \tag{14}$$

Table I
Values of ΔG and x_{cis} for Polymerization of Cyclopentene

t, °C	ΔG_{cis}, kJ/mol	ΔG_{trans}, kJ/mol	x_{cis} (eq 20)	ΔG_{lc}, kJ/mol eq 8 or 16	eq 2
30	1.0	-2.5	0.20	-3.1	-1.8
20	0.5	-3.2	0.18	-3.7	-2.5
10	0.0	-4.0	0.16	-4.4	-3.4
0	-0.5	-4.8	0.13	-5.1	-4.2
-10	-1.0	-5.5	0.11	-5.7	-5.0
-20	-1.5	-6.2	0.10	-6.4	-5.7
-30	-2.0	-7.0	0.08	-7.1	-6.6
-40	-2.6	-7.7	0.07	-7.8	-7.3
-50	-3.8	-8.4	0.08	-8.6	-8.0

which is solved for $K = 1$. With this value of K, from eq 3, 9, and 10, it follows that

$$x_{cis} + x_{trans} = \exp(X) + \exp(Y) = 1 \quad (15)$$

or more explicitly, using eq 9–11

$$\ln [\exp(-\Delta G_{cis}/RT) + \exp(-\Delta G_{trans}/RT)] = -(\overline{\Delta G}_m - \overline{\Delta G}_p)/RT = -(\Delta G_{lc}/RT) \quad (16)$$

The right-hand side of eq 16 simply follows from eq 12. Since there is only one monomer involved in the polymerization and if interactions between cis and trans units and other species are considered to be the same, then eq 1 applies and eq 16 becomes

$$-\ln [\exp(-\Delta G_{cis}/RT) + \exp(-\Delta G_{trans}/RT)] = \ln \phi_m + 1 + \phi_s(\chi_{ms} - \chi_{sp}(\bar{V}_m/\bar{V}_s)) + \chi_{mp}(\phi_p - \phi_m) \quad (17)$$

Upon examination of eq 1, 2, 8, and 17, it is found that $\Delta G_{lc}/RT$ determines the amount of monomer and polymer present at equilibrium together with the interaction parameters. However, ΔG_{lc} is not the result of additive contributions from ΔG_{cis} and ΔG_{trans} as stated by eq 2 but rather obeys the more complex relationship of eq 8 or 16. Equation 17 shows that the knowledge of x_{cis} and x_{trans} is not required to compute the amount of monomer and polymer present at equilibrium.

The proportions of cis and trans found in the polymer are obtained from eq 9 and 10. With eq 11 and 12, one can write

$$x_{cis} = \exp(\Delta G_{lc} - \Delta G_{cis})/RT \quad (18)$$

$$x_{trans} = \exp(\Delta G_{lc} - \Delta G_{trans})/RT \quad (19)$$

Solving for ΔG_{lc} and substituting into eq 8 one obtains

$$(\Delta G_{cis} - \Delta G_{trans})/RT = \ln [(1 - x_{cis})/x_{cis}] \quad (20)$$

Equation 20 shows that the proportion of cis and trans in the polymer is independent of the medium of the polymerization whereas the amounts of monomer and polymer found at equilibrium depend together on ΔG_{cis}, ΔG_{trans} and the medium through the χ parameters (eq 17). It is also found that, at a given temperature, there is only one possible composition if the reaction is thermodynamically controlled.

Polymerization of Cyclopentene

The above equations can be applied to the polymerization of cyclopentene. The metathesis polymerization of this monomer leads to an equilibrium between the monomer and the active polymer.[1-3] In order to verify the equations, one needs to know the values of ΔG_{cis} and ΔG_{trans}. These values can be computed from the heats and entropies of formation of monomer and polymer obtained through a semiempirical method. Values of ΔG_{cis} and ΔG_{trans} computed in this manner[8] for the -50 to 30 °C temperature range are shown in Table I. These values differ by approximately 1 kJ from published results.[9,10]

Table II
Polymerization of Cyclopentene with Nonstereospecific Catalysts

catalytic system	t, °C	x_{cis} obsd	calcd	ref
$WCl_6 + Al(C_2H_5)_3$	-30	0.10	0.08	12
$WCl_6 + C_2H_5OH + Al(C_2H_5)Cl_2$	0	0.16	0.13	13
$WCl_6 + C_2H_4ClOH + Al(C_2H_5)Cl_2$	0	0.16	0.13	13
$WCl_6 + (CN)C_2H_4OH + Al(C_2H_5)Cl_2$	0	0.16	0.13	13
$WCl_6 + C_2H_5OH + Al(C_2H_5)Cl_2$	0–30	0.10–0.30	0.13–0.20	2
$WCl_6 + (C_2H_5)_2O + Sn(C_2H_5)_4$	0–30	0.20	0.13–0.20	11
$(CO)_5W[C(OC_2H_5)C_4H_9] + TiCl_4$	5	0.19	0.15	14
$WCl_6 + C_2H_5OH + Al(C_2H_5)_2Cl$	20	0.10–0.15	0.18	15
$WCl_6 + C_6H_5OH + Al(C_2H_5)_2Cl$	20	0.15–0.25	0.18	15
$WCl_6 + C_6H_5OH + Al(C_2H_5)Cl_2$	20	0.20–0.25	0.18	15
$(CO)_5W[C(OC_2H_5)C_4H_9] + Al(C_2H_5)Cl_2$	20	0.14	0.18	14
$(CO)_5W[C(C_6H_5)_2] + TiCl_4$	20	0.12–0.17	0.18	14
$(CO)_5W$(piperidine) $+ TiCl_4$	20	0.14	0.18	14
$(CO)_5W$(ethylamine) $+ TiCl_4$	20	0.15	0.18	14
$[(CO)_5WCOC_6H_5]^-[N(CH_3)_4]^+ + Al(C_2H_5)Cl_2$	20	0.10	0.18	19
$MoCl_3(C_{17}H_{35}COO)_2 + Al(C_2H_5)_2Cl$	25	0.20–0.22	0.19	16
$H_2WO_4 + AlCl_3$	25	0.17	0.19	17
$H_2WO_4 + AlCl_3 +$ epichlorohydrin	25	0.17	0.19	17

Table III
Polymerization of Cyclopentene with Stereospecific Catalysts

catalytic system	t, °C	x_{cis}	ref
$WCl_6 + (C_2H_5)_2O + Sn(C_2H_5)_4$	-70 to -30	0.92	11
$WCl_6 + Si(C_3H_5)_4$	-50 to -10	0.01	1
$TiCl_4 + Al(C_2H_5)_3$	-30	0.03	12
$MoCl_5 + Al(C_2H_5)_3$	-30	0.99	12
$WF_6 + Al(C_2H_5)Cl_2$	0	0.95	13
$(CO)_5W[C(C_6H_5)_2]$	40	0.95	18

With the use of eq 20 and the data of Table I, values of x_{cis} are readily obtained and are listed in Table I. These values can be compared with the results obtained for polymerizations with various catalysts. If the catalysts are stereospecific, one would expect polymer with either cis or trans configuration near 100%. On the other hand, if the catalysts are not stereospecific and if the polymerization is thermodynamically controlled, the compositions should compare with x_{cis} listed in Table I. Table II shows experimental results, with the computed value in brackets, obtained at various temperatures with catalysts which are not considered to be stereospecific. The agreement is fairly good considering the large variety of catalytic systems involved and the possibility of fairly large experimental errors. Table III shows the results obtained with systems which can be considered as stereospecific. It should be pointed out that cis polymer can be obtained although less favored by thermodynamics than trans polymer and that systems may be stereospecific at low temperature and lose their stereospecific property at higher temperature.[1,11]

ΔG_{cis}, ΔG_{trans}, and x_{cis} being known, ΔG_{lc} follows from eq 8 or 16. Since x_{cis} is unique at a given temperature, both eq 8 and 16 yield the same result for ΔG_{lc}. The importance of the ΔG_D term introduced in eq 4 can be evaluated through comparison of ΔG_{lc} obtained from eq 2 and 16 (or eq 8). The values of ΔG_{lc} are shown in Table I and their

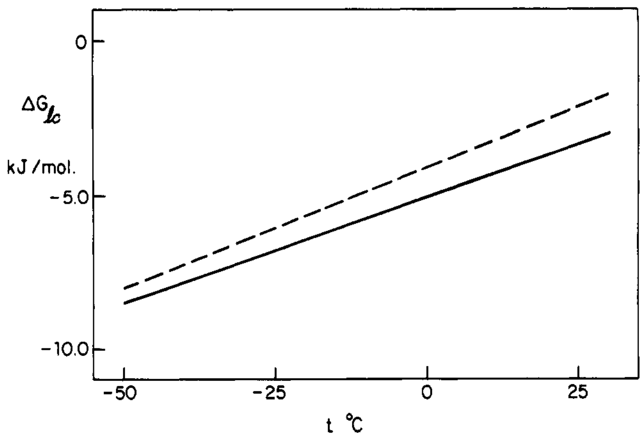

Figure 1. Variation of ΔG_{lc} with temperature: according to eq 2, broken line; according to eq 16, full line.

Table IV
Polymerization of Cyclopentene in Benzene (from 0 to 30 °C) and Toluene (from -50 to -10 °C)

t, °C	% cis	ϕ_m	ϕ_p	ref
30	10–30	0.11	0.09	2
20	10–30	0.08	0.11	2
10	10–30	0.06	0.12	2
0	10–30	0.04	0.14	2
-10	94–98	0.28		1, 3
-20	94–98	0.18	0.20	1, 3
-30	94–98	0.14	0.06	1, 3
		0.14	0.16	
		0.13	0.26	
-40	94–98	0.10	0.10	1, 3
-50	94–98	0.07	0.15	1, 3

variation with temperature according to eq 2 and 16 is plotted in Figure 1.

The differences observed in values of ΔG_{lc} depending on the equations used take all their significance in the computation of the equilibrium monomer concentration, or the equilibrium monomer volume fraction ϕ_m. ϕ_m is computed with eq 1 or its linear form[4]

$$\phi_m = -\frac{(\Delta G_{lc}/RT) + \ln \phi_m^0 + \beta}{\beta + \chi_{mp} - 1/\phi_m^0} + \frac{\chi_{mp} - \beta}{\beta + \chi_{mp} - 1/\phi_m^0}\phi_p \qquad (21)$$

where $\beta = \chi_{ms} - \bar{V}_m/\bar{V}_s$ and ϕ_m^0 is equal to ϕ_m when $\phi_p \rightarrow 0$. Because the values of the χ parameters are not known for the cyclopentene polymerization system, values of parameters of systems closely related to it are used instead. The values are as follows: $\chi_{mp} = 0.21$ for the cyclohexane–polybutadiene system;[20] $\chi_{sp} = 0.23$ for the benzene–polybutadiene system;[21] $\chi_{ms} = 0.24$ for the cyclohexane–benzene system.[22] Values of ΔG_{lc} are obtained from Table I and ϕ_m is computed for various ϕ_p according to eq 1 (or 21) using an iterative method. The variation of ϕ_m and ϕ_p at various temperatures is shown in Figure 2 and compared with experimental results given in Table IV. The experimental results can be divided into two sets of data. From Table IV it is quite obvious that in the 0–30 °C temperature range the results have been obtained with nonstereospecific catalysts. These results can be compared with ϕ_m computed from ΔG_{lc} shown in Table I. In order to check the relevance of ΔG_D introduced in eq 4, values of ΔG_{lc} obtained from either eq 2 or 16 (or eq 8) are used for the computation of ϕ_m. From Figure 2a it is quite clear that the agreement is much better if eq 16 is used rather than eq 2 even with the use of the cis percentage that would yield the best agreement (with 10% cis, ϕ_m would be equal to 0.16 at 30 °C). In the -10 to -50 °C temperature range, the polymerization is stereospecific with a proportion of cis configuration near 100%. In this case ΔG_{lc} is set equal to ΔG_{cis}, ϕ_m is computed with eq 1 or 21, and the results are shown in Figure 2b. Except for the two extreme temperatures where the experimental ϕ_m is much higher than expected (see Table IV), the agreement is good. Any other value of ΔG_{lc} from Table I would yield a value of ϕ_m around 4×10^{-3}. Equation 1 can also be used to compute ϕ_m in the case of bulk polymerization ($\phi_s = 0$). For the isotactic polymerization of cyclopentene at 0 °C, from ΔG_{cis} of Table I, a value of 0.25 is obtained for ϕ_m compared with the experimental value of 0.29.[23] These results show that, although the configuration of the polymer is not controlled by thermodynamics, the equilibrium between monomer and polymer depends on the configu-

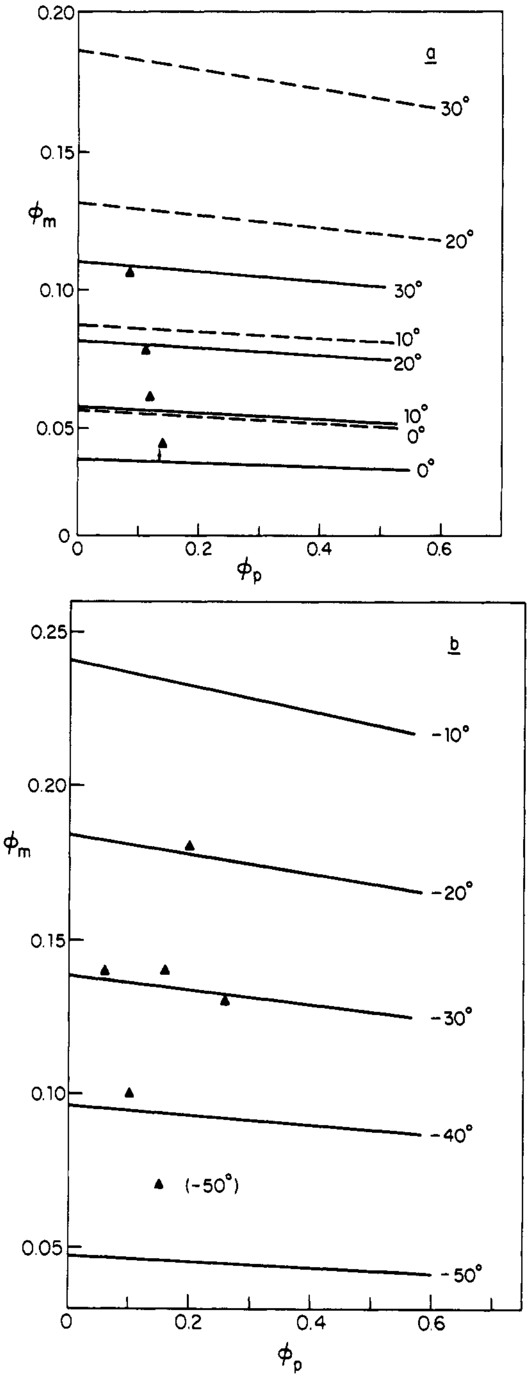

Figure 2. Polymerization of cyclopentene. Variation of ϕ_m with ϕ_p at various temperatures. Triangles: experimental values. a: Nonstereospecific polymerization in benzene. Broken line, using eq 2; full line, using eq 16. b: Stereospecific polymerization in toluene. Full line, using eq 1 or 21 for 100% cis.

ration of the polyalkenamer thus formed.

Conclusion

When a polymerization leads to the formation of a polyalkenamer, two situations may arise. In the first case the polymerization is stereospecific and polymer with near 100% cis or trans configuration is obtained. In the second case the polymerization is not stereospecific and the configurations of the monomer units are not totally cis or trans. The present paper shows that in the latter case a term ΔG_D ought to be introduced in the expression of ΔG_{lc}. This term takes into consideration the fact that the polymer is made of two types of distinguishable units. Moreover, it is concluded that, if the formation of the polymer is thermodynamically controlled, the composition of the polymer is unique, which is in agreement with the results obtained for the polymerization of cyclopentene. If a monomer–polymer equilibrium exists, it is also found that the amount of monomer present under equilibrium condition is dependent on the configuration of the polymer. This is observed even if the configuration of the polymer thus formed is not controlled by thermodynamics as it is the case for the conversion of cyclopentene into near 100% *cis*-polypentenamer.

Acknowledgment. We acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada.

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Amino Acid Sequence Determination for Sequential Polypeptides Consisting of γ-Benzyl and γ-Methyl L-Glutamates by ^{1}H and ^{13}C NMR Methods

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ABSTRACT: A series of sequential polypeptides consisting of γ-benzyl L-glutamate (B) and γ-methyl L-glutamate (M) prepared by the fragment self-condensation method using the dicyclohexylcarbodiimide/*N*-hydroxysuccinimide (DCC/HONSu) activated ester method were measured in trifluoroacetic acid (TFA) and TFA/$CDCl_3$ (1:1) solutions by means of 100-MHz ^{1}H, 500-MHz ^{1}H, 25-MHz ^{13}C, and 125-MHz ^{13}C NMR spectrometers. It was found from these observations that the amino acid sequence determination for these copolymers is well established on the basis of a definite distribution of the hexad (or pentad) sequence of B and M in the chain. In the ^{1}H NMR observations, the hexad and also higher order sequence effects, probably caused by the ring current effect of side-chain phenyl groups, were revealed for the OCH_3 proton peak of the M residue in the copolymers. On the other hand, in the ^{13}C NMR, the pentad and/or higher order sequence effects were revealed for the $C{=}O_{ester}$ and C_α peaks of the M residue and for all the peaks (except for C_{phenyl}) of the B residue in the copolymers.

Introduction

High-resolution NMR spectroscopy has provided very useful information about the stereochemical structure of polymers.[1] Such information sometimes permits a definite determination of possible structures to be made. For proteins, knowledge of the primary structure of the peptide chains is critical for many biochemical and biophysical studies. At present, amino acid sequence determination is well established and this is almost a routine procedure for many smaller proteins.[2] NMR proves to be a very