Heats of Mixing at Infinite Dilution of Atactic Polymers. 2. Effect of the Steric Hindrance and of the Shape of the Solvent

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Received March 9, 1979

ABSTRACT: Heats of (A) polybutene-1, polypropylene, polyisobutylene, poly(dimethylsiloxane), (B) polypentenamer, polybutadiene, and (C) three ethylene–propylene copolymers in (1) three cycloalkanes, (2) *cis*- and *trans*-bicyclo[4.4.0]decane, (3) six-branched heptanes, and (4) three-branched nonanes have been measured at infinite dilution (h_∞^E) at 25 °C in a Tian–Calvet microcalorimeter. A negative, non-free-volume contribution found in nonpolar small molecule systems when one of the components is sterically hindered (br-C_7 and br-C_9) or has a special shape (c-C_5 and *trans*-decalin) was investigated in the case of a polymeric second component. The Flory equation of state has been used to calculate the free-volume term and obtain, from h_∞^E, the $X_{12}s_1^{-1}$ parameter which corresponds to the non-free-volume contribution. In nonordered solutions (PBu-1, PP, Cop 33% E), the $X_{12}s_1^{-1}$ are mostly <0 due to the dominance of the steric hindrance and shape contribution. In the other solutions, force-field difference (PDMS), order in the polymer and force-field difference (PBD, PPmer, Cop 63% E, Cop 75% E), or overestimation of the free volume (PIB) make the $X_{12}s_1^{-1} > 0$. However, the steric hindrance or shape contribution can be evaluated by the spread of the $X_{12}s_1^{-1}$ between isomers in a series. It is found that the spread is of similar magnitude (−2 to −6 J cm^{-3} Å) for the ordered or not ordered polymers but higher (−4 to −8 J cm^{-3} Å) for the copolymers. These values are in the range of those found in small molecule mixtures. The finding that homopolymers and small molecule mixtures show effects of similar magnitude presents an interest of a fundamental character for the study of nonpolar interactions in solution. The easy recovery of expansive isomers in polymeric mixtures is worthwhile mentioning. h_∞^E may be used to dose the ethylene content of the copolymers.

In part 1 of this work, h_∞^E has been measured for three types of polymers: four polymers made of branched segments (A), two polymers with linear segments (B), and three copolymers consisting of branched and linear segments. The relative values of the heats in branched and linear alkanes were interpreted in terms of order–disorder, i.e., either of destruction or of formation of correlations of molecular orientations between the two components of the solutions. By analogy with previous results obtained on mixtures of small alkane-like molecules[2-4] showing the loss of orientational order when methyl groups replace H atoms along the chain, the assumption was made that correlations of orientations occurred almost exclusively between pairs of the ($-CH_2CH_2-$) and ($CH{=}CH-)_n$ groups but not between pairs of the ($-CH_2CH(R)-$) or (CH_2-C-$(R)_2-$) groups. This assumption seemed to be justified by the results.

The branched solvents were chosen, in part 1, in order to be as similar to each other as possible and to contrast between linear and branched solvents. However, effects on the heats of rather small differences in the shape of the polymer segment could be seen for instance by the different h_∞^E in n-C_{16} of the various polyolefins, the heat being particularly low with the highly sterically hindered PIB segment. As the choice of commercialy available branched solvents is wider than that of branched atactic polymers, the study of branching of one component was more easily achieved by using differently branched segments in the solvent.

The Steric Hindrance Effect. Effect on the Heats of Mixing. The branched alkanes and other molecules used in this study have already been investigated in mixtures with small molecules. The steric hindrance effect was first noticed when heats of mixing of nonpolar systems were obtained and discovered to be either too negative or positive but not large enough to meet the expected value. Such a molecule is 3,3-diethylpentane (DEP) whose H_M^E with n-C_8[6] (−80 J mol^{-1}) cannot at all be explained by the difference between the free volumes of the components. H_M^E is the maximum value of H^E in the H^E vs. composition plot. Recent measurements[7] of the H_M^E of DEP have shown that they are negative with many other second components. In other branched alkane mixtures, heats of mixing and consequently steric hindrance are very sensitive to the position of the methyl groups along the chain. For example, while 2,2-dimethylpentane and 2,4-dimethylpentane do not appear sterically hindered, the reverse is true for 2,3-dimethylpentane and 3,3-dimethylpentane. Experimental data on the heats of branched heptanes and branched nonanes with long-chain compounds, where the heats are not negative but are much lower than the expected value, can be found in ref 7 and 9. It is worth noting that the compound $Sn(C_2H_5)_4$ has structural features similar to DEP [DEP can be written $C(C_2H_5)_4$], and it too shows unexpected low heats [$Sn(C_2H_5)_4$ + br-C_{16} = −80 J mol^{-1}][10]. To account for the negative sign of the H_M^E or their too low values, this new contribution to the heats of mixing has been named condensation or steric hindrance contribution,[11] the effect corresponding to the heat having the same name. It is analogous to an order formation in solution but cannot, however, be visualized as simply as that due to the correlations of orientations or good fitting of the ethylene segments investigated in part 1. It may be related to lower mobility in the solution or change in the vibration and rotational modes either of the sterically hindered compound or of the second component or of both.

Effect on the Free Energies of Mixing. Only a few free-energy measurements have been made on mixtures of small molecules whose H_M^E showed the negative steric hindrance contribution. The vapor pressure measurements of solutions in long chain alkanes of DEP[6] and of several branched alkanes[9] with various degrees of steric hindrance showed that, at the concentration of the maximum, there was a partial compensation between the enthalpic and entropic contributions due to steric hindrance. Consequently, the total steric hindrance effect on the free energy is small.

In the case of polymer solutions, the effect of steric hindrance on free energies of mixing was measured indirectly by intrinsic viscosities. It was found then that, at infinite dilution of the polymer, i.e., in solutions rich in the sterically hindered compound, the free energy was

0024-9297/79/2212-0746$01.00/0

considerably lowered[10] (in other words, the intrinsic viscosity was increased). Another indication of the higher solubility of polymers in sterically hindered solvents is given by their lower critical solubility temperature (LCST). The LCST of PIB in the more sterically hindered 2,3-dimethylpentane is 50 °C higher than that obtained with the 2,4-dimethylpentane.[11]

Compounds in the SnR_4 series[12,13] and to a lesser extent in the NR_3 series,[12,14] in solution with a long chain second component such as the linear alkanes, show the steric hindrance effect. However, results of h_∞^E of the polymers in these solvents are not reported here but will be published later.

Specific Effect of the Solvent Molecular Shape. Cycloalkanes. Heats of mixing of small molecules with the cycloalkanes series[15] on the one hand and the two isomers of bicyclo[4.4.0]decane on the other[16,17] indicate that a negative contribution occurs for cyclopentane and the two isomers. It was found, however, that with most second components the trans isomer of bicyclo[4.4.0]decane gives a more negative or less positive H_M^E. Measurements of intrinsic viscosities of ethylene–propylene copolymers showed that the free energy of mixing was lowered in these solvents,[10] but its extent in the bicyclo[4.4.0]decane isomers was sensitive to the polymer degree of branching, i.e., to its composition. In this work, h_∞^E of homopolymers and copolymers has been measured in the different cycloalkanes in order to obtain information on the role of the low free volume of the polymer and of the high dilution in one component on the negative shape contribution to the heats and free energies.

h_∞^E has been obtained for the following systems: (1) the cycloalkane series c-C_5 to c-C_8 (except c-C_7) and the A, B, and C polymers, (2) *cis*- and *trans*-bicyclo[4.4.0]decane and the A, B, and C polymers, (3) three branched nonanes, one not sterically hindered, 2,2,4,4-tetramethylpentane, and two sterically hindered, 2,3,3,4-tetramethylpentane and 3,3-diethylpentane, and the A, B, and most of the C polymers, and (4) six branched heptanes of increasing degree of steric hindrance, 2,2-dimethylpentane, 2,4-dimethylpentane, 3-methylhexane, 3-ethylpentane, 3,3-dimethylpentane, and 2,3-dimethylpentane, and the A, B, and C polymers. As in part 1, the A polymers are the order breakers, polyisobutylene (PIB), polypropylene (PP), polybutene-1 (PBu-1), and poly(dimethylsiloxane) (PDMS). The B polymers, polybutadiene (PBD) and polypentenamer (PPmer), have some degree of order. The C polymers are the three ethylene–propylene copolymers. The commercial name of bicyclo[4.4.0]decane is decalin, and this will be used in the following text. 3,3-Diethylpentane has been shortened to DEP.

Experimental Section

Apparatus. The heats were measured with a tilting Tian-Calver calorimeter. Details on the apparatus and on the technique are given elsewhere.[1,18]

Polymers. The atactic polymers were obtained from different companies[1] and were used without purification. PBu-1 and PP were extracted from the isotactic material.

Solvents were purchased from either the Aldrich Co. (Milwaukee) or the Chemical Sample Co. (Columbus, Ohio) and were used without purification except in the case of one branched C_7 and two branched C_9 which, before purification, would give a slight reaction with mercury.

Theory

The heats of mixing at infinite dilution are obtained from the experimental heats h_{exptl}^E, the polymer volume fraction ϕ_2, and its density d_2 by the relation:

$$h_\infty^E = h_{\text{exptl}}^E d_2/(1 - \phi_2)$$

In a formal way, one can write the experimental heat of mixing as the sum of four contributions even if it is not proven that they are additive and independent.

$$h_\infty^E = h_{\text{chem}}^E + h_{\text{dis}}^E + h_{\text{sh}}^E + h_{\text{f.v.}}^E \qquad (1)$$

h_{chem}^E and h_{dis}^E are positive and are due respectively to the difference in force fields and orientational order of the two compounds mixed. $h_{\text{f.v.}}^E$ has its origin in the difference in free volume of the solvent and the polymer. It is negative and largest in the nonexpanded polymer (PIB)–volatile solvent (c-C_5) systems. It can be calculated by equation of state theories. h_{sh}^E (sh is steric hindrance) is the negative contribution particularly studied in this paper. In the Prigogine theory,[19] parameters of size and energy differences between the polymer and the solvent would enter that part of the heat which is not produced by the free-volume difference. In the Flory theory,[20] the non-free-volume contributions are assembled in the X_{12} parameter obtained by the difference between the experimental heat and the free-volume term, $g(\alpha_1,\alpha_2)$.

$$h_\infty^E = X_{12} f(\tilde{v}_1, P_2^*) + g(\alpha_1,\alpha_2) \qquad (2)$$

The detailed expression of the free-volume term where α_1 and α_2 are the expansion coefficients of the two components has been fully defined in part 1.

Comparison of the Heats for Isomers. As the isomers have the same groups and state of expansion, the variation of the experimental heats will not come from different values of $h_{\text{f.v.}}^E$ or h_{chem}^E or h_{dis}^E but more likely will come from a difference in magnitude of h_{sh}^E. Since h_{sh}^E is negative, h_∞^E will become less positive or more negative for increasing steric hindrance of the isomer. X_{12} will follow the same trend, a negative value of which reflects the preponderance of the h_{sh}^E contribution.

Physicochemical Data on the Pure Components. Table I gives the values of the densities, expansion coefficients, core volume, pressure reduction parameter, and surface to volume ratio of the solvents and polymers. Details about the calculation or the original data can be found in ref 10.

Results and Discussion

Comparison of the heats for the different compounds in the same category can be done either on h_∞^E or on X_{12}. It has been shown many times that the X_{12} values obtained in systems with large free-volume differences are too large because $h_{\text{f.v.}}^E$ is calculated to be too negative. This is the case of PIB with the lower alkanes[18] ($\alpha = 0.55 \times 10^{-3} K^{-1}$) but not of PDMS ($\alpha = 0.89 \times 10^{-3} K^{-1}$). The comparison of the cyclic alkane results will be made on both h_∞^E and X_{12}. However, for the branched heptanes, branched nonanes, and *cis*- and *trans*-decalin, comparison of the X_{12} only will be necessary since the difference in expansion coefficients inside the group of br-C_7 and br-C_9 is small, thus the overestimation of $h_{\text{f.v.}}^E$ is about the same for the isomers.

Table II gives the experimental and calculated parameters for all the systems, i.e., h_∞^E, $X_{12}s_1^{-1}$, and $h_{\text{f.v.}}^E$. In order to facilitate reading of the tables and comparing the different polymers and in order to spot systems with negative X_{12} values, the range of the X_{12} parameters has been marked on Figure 1 for all the polymers. Exact values of X_{12} for systems presenting a special interest, such as those with c-C_5 and *cis*- and *trans*-decalin, have been identified, while systems in a series are shown by a line drawn between the extreme values.

Cycloalkanes. Benson and Coll[17] have found that the H_M^E of c-C_5 with toluene is about 250 J mol^{-1} lower than

Table I
Parameters of the Pure Compounds

compd	$d_{298\ \mathrm{K}}$, g cm^{-3}	$10^3\alpha_{298\ \mathrm{K}}$, K^{-1}	V^*, cm^3 mol^{-1}	P^*, J cm^{-3}	$s = S/V$, Å^{-1}
cyclopentane	0.7404	1.332	72.2	509	0.89
cyclohexane	0.7739	1.217	84.3	530	0.93
cyclooctane	0.8320	0.986	108.3	563	0.99
cis-bicyclo[4.4.0]decane	0.8929	0.851	127.3	542	0.95
trans-bicyclo[4.4.0]decane	0.8659	0.865	130.9	504	0.88
2,2-dimethylpentane	0.6695	1.294	114.7	394	1.03
2,4-dimethylpentane	0.6683	1.313	114.6	407	1.04
3-methylhexane	0.6830	1.224	113.6	418	1.04
3-ethylpentane	0.6940	1.220	112.9	434	1.00
3,3-dimethylpentane	0.6891	1.218	112.7	415	1.04
2,3-dimethylpentane	0.6909	1.209	112.5	428	1.04
2,2,4,4-tetramethylpentane	0.7156	1.075	141.9	376	0.79
2,3,3,4-tetramethylpentane	0.7511	0.958	137.8	390	0.79
3,3-diethylpentane	0.7500	0.957	138.0	422	0.78
PIB	0.917	0.555	1.129	447	0.58
PBu-1	0.870	0.700	0.972	418	0.47
PDMS	0.969	0.887	0.897	353	0.60
PPmer	0.889	0.702	0.951	497	0.90
PBD	0.905	0.685	1.144	502	1.00
PE	0.855	0.752	0.979	484	0.80
PP	0.858	0.806	0.966	470	0.70
Cop 33% E	0.856	0.780	0.973	475	0.73
Cop 63% E	0.857	0.772	0.973	489	0.76
Cop 75% E	0.858	0.765	0.973	481	0.77

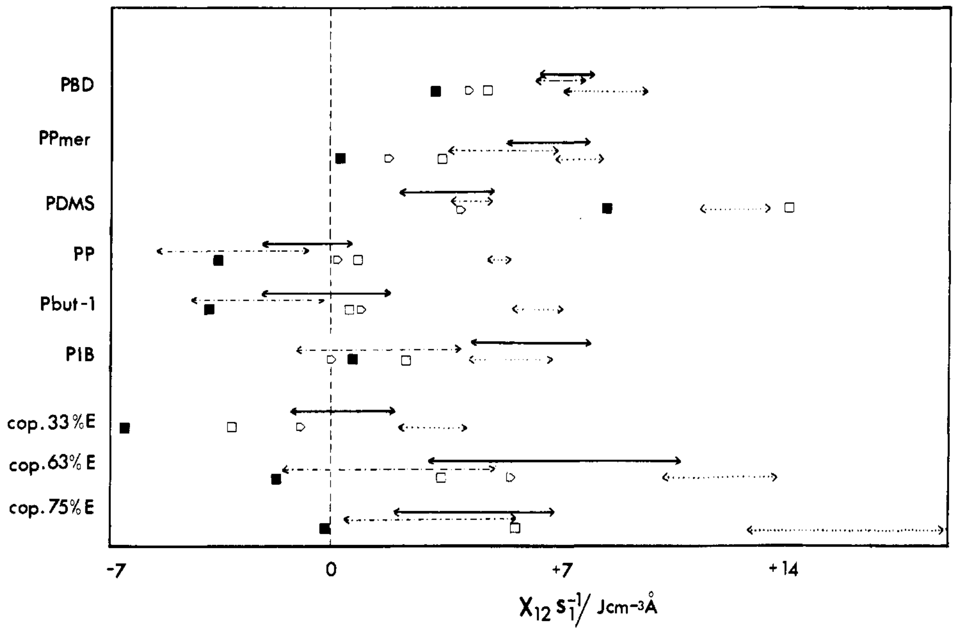

Figure 1. $X_{12}s_1^{-1}$ values in J cm^{-3} Å for the polymers in the different series. The ranges are marked for the three series br-C$_7$ (—), br-C$_9$ (- - -), and c-C$_n$ (···). For three compounds, c-C$_5$ (□), and *cis*- (□) and *trans*- (■) decalin, individual values have been plotted. $X_{12}s_1^{-1}$ is negative for most of the polymers with *trans*-decalin. Data for PIB are displaced toward higher values due to an overestimation of the free volume term. The steric hindrance effect of some branched alkanes can be seen either from the negative $X_{12}s_1^{-1}$ or on the spread of the positive $X_{12}s_1^{-1}$ for polymers having a force field difference with the solvent (PDMS), or with some orientational order (copolymers), or both (PBD and PPmer). The c-C$_5$ effect gives a much lower value for c-C$_5$ than for the other c-C$_n$'s. Negative values found with linear alkanes in part 1 are not plotted here.

those with the other cycloalkanes. The difference between H_M^E(c-C$_5$) and H_M^E(c-C$_6$) is large again (−200 J mol^{-1}) when the second component is either 2,3-dimethylbutane[16] or 2,2,5-trimethylhexane.[21] Patterson et al.[8] report a difference of almost −300 J mol^{-1} when the second component is the sterically hindered DEP. C_P^E is positive, whereas nonpolar mixtures almost invariably give negative C_P^E. These authors suggest that the anomalous results in H_M^E(−), C_P^E(+), and dC_P^E/dT(−) are due to a hindering of the rotation of the platelike c-C$_5$ molecules by the anisotropic second component. The present measurements aim at finding out if a polymeric second component has the same effect on c-C$_5$ as does a small molecule and whether the special conditions of the polymer solution, i.e., low free volume of the second component and high concentration of c-C$_5$, influence the magnitude of this shape effect.

Figures 2a,b and 2c,d show respectively h_∞^E and $X_{12}s_1^{-1}$ for all the polymers vs. the core volume of the cycloalkane. One sees indeed a large diminution of both h_∞^E and $X_{12}s_1^{-1}$ for c-C$_5$ compared with the other cycloalkanes. $X_{12}s_1^{-1}$ is <0 for Cop 33% E and near 0 for PIB, PP, and PBu-1. In order to compare the magnitude of the effect with that occurring in mixtures with a small molecule second component, the difference between $X_{12}s_1^{-1}$ (c-C$_5$) and $X_{12}s_1^{-1}$ (c-C$_6$) has been listed in the second column of Table

Table II

Heats of Mixing at Infinite Dilution of Nine Polymers in (1) Three Cycloalkanes, (2) *cis*- and *trans*-Decalin, (3) Seven Branched Heptanes, and (4) Three Branched Nonanes at 298

	order-breaker polymers (2)														
	PIB			PBu-1			PP			PDMS			Cop 33% E (67% P)		
solvent (1)	$h_\infty{}^{E}$, J g^{-1}	$X_{12}/s_1{}^{1}$, J cm^{-3} Å	$h_{f.v.}{}^{E}$, J g^{-1}	$h_\infty{}^{E}$, J g^{-1}	$X_{12}/s_1{}^{1}$, J cm^{-3} Å	$h_{f.v.}{}^{E}$, J g^{-1}	$h_\infty{}^{E}$, J g^{-1}	$X_{12}/s_1{}^{1}$, J cm^{-3} Å	$h_{f.v.}{}^{E}$, J g^{-1}	$h_\infty{}^{E}$, J g^{-1}	$X_{12}/s_1{}^{1}$, J cm^{-3} Å	$h_{f.v.}{}^{E}$, J g^{-1}	$h_\infty{}^{E}$, J g^{-1}	$X_{12}/s_1{}^{1}$, J cm^{-3} Å	$h_{f.v.}{}^{E}$, J g^{-1}
cyclopentane	−5.9	+0.0	−5.9	−2.9	+0.9	−3.4	−2.3	+0.2	−2.4	+1.0	+3.9	−1.1	−3.5	−0.9	−2.8
cyclohexane	−0.6	+6.5	−4.4	+1.0	+6.9	−2.3	+2.3	+5.3	−1.5	+5.2	+11.0	−0.6	+1.4	+4.0	−1.8
cyclooctane	+0.3	+4.1	−2.0	+1.8	+5.4	−0.8	+3.0	+4.7	−0.3	+6.8	+13.0	−0.1	+1.2	+2.1	−0.4
cis-bicyclo[4.4.0]decane	+0.2	+2.2	−1.0	<0.1	+0.5	−0.2	+0.5	+0.8	0.0_2	+7.1	+13.7	-0.0_3	−2.4	−2.9	−0.1
trans-bicyclo[4.4.0]decane	−0.8	+0.6	−1.1	−2.0	−3.6	−0.3	−2.4	−3.3	0.0_4	+4.3	+8.2	-0.0_1	−4.8	−6.1	−0.1
2,2-dimethylpentane	−1.1	+7.3	−5.4	−4.0	−2.0	−3.0	−2.2	−0.1	−2.1	+0.8	+3.2	−0.9			
2,4-dimethylpentane	−1.1	+7.7	−5.7	−2.3	+1.8	−3.2	−1.8	+0.6	−2.3	+1.6	+4.8	−1.0	−1.2	+1.8	−2.6
3-methylhexane	−1.0	+6.0	−4.5	−2.1	+0.5	−2.4	−1.8	−0.2	−1.6	+1.3	+3.6	−0.6			
3-ethylpentane	−2.0	+4.3	−4.5	−2.8	−1.0	−2.4	−2.5	−1.4	−1.6	+0.6	+2.3	−0.6			
3,3-dimethylpentane	−1.7	+4.8	−4.4	−2.2	+0.3	−2.3	−3.0	−2.0	−1.5	+0.5	+2.1	−0.6	−2.7	−1.3	−1.8
2,3-dimethylpentane	−1.9	+4.2	−4.4	−2.8	−1.0	−2.3	−2.5	−1.4	−1.5	+1.4	+3.7	−0.6			
2,2,4,4-tetramethylpentane	−0.6	+3.9	−2.9	−1.4	−0.2	−1.3	−0.8	−0.7	−0.2	+2.3	+4.8	−0.2			
2,3,3,4-tetramethylpentane	−2.3	−0.9	−1.8	−2.2	−3.2	−0.6	−3.1	−4.0	−0.2	+1.9	+3.6	-0.0_3			
3,3-diethylpentane	−1.4	+0.7	−1.8	−2.6	−4.1	−0.6	−3.9	−5.2	−0.2	+1.9	+3.6	-0.0_3			

	ordered or potentially ordered polymers											
	PPmer			PBD			Cop 63% E (37% P)			Cop 75% E (25% P)		
solvent	$h_\infty{}^{E}$, J g^{-1}	$X_{12}/s_1{}^{1}$, J cm^{-3} Å	$h_{f.v.}{}^{E}$, J g^{-1}	$h_\infty{}^{E}$, J g^{-1}	$X_{12}/s_1{}^{1}$, J cm^{-3} Å	$h_{f.v.}{}^{E}$, J g^{-1}	$h_\infty{}^{E}$, J g^{-1}	$X_{12}/s_1{}^{1}$, J cm^{-3} Å	$h_{f.v.}{}^{E}$, J g^{-1}	$h_\infty{}^{E}$, J g^{-1}	$X_{12}/s_1{}^{1}$, J cm^{-3} Å	$h_{f.v.}{}^{E}$, J g^{-1}
cyclopentane	−2.3	+1.8	−3.9	<0.1	+4.1	−4.1	+1.1	+5.3	−2.9	ins		
cyclohexane	+4.6	+8.0	−2.7	+5.4	+8.3	−2.9	+8.1	+13.2	−1.9	+11.8	+18.3	−2.0
cyclooctane	+5.1	+6.7	−0.9	+5.8	+6.9	−1.0	+6.9	+9.9	−0.5	+8.6	+12.4	−0.5
cis-bicyclo[4.4.0]decane	+2.6	+3.3	−0.3	+4.2	+4.7	−0.3	+2.4	+3.3	-0.0_7	+3.9	+5.5	-0.0_8
trans-bicyclo[4.4.0]decane	<0.1	+0.3	−0.3	+2.6	+3.1	−0.4	−1.3	−1.7	-0.0_9	−0.3	−0.2	−0.1
2,2-dimethylpentane	+3.3	+7.4	−3.5	+4.1	+7.8	−3.7	+5.3	+10.4	−2.6	+2.3	+6.6	−2.6
2,4-dimethylpentane	+3.3	+7.6	−3.7	+3.2	+7.2	−3.9	+3.0	+7.5	−2.8	+0.2	+4.0	−2.8
3-methylhexane	+2.4	+5.7	−2.8	+3.6	+6.6	−3.0	+0.7	+3.5	−2.0	+1.7	+5.0	−2.0
3-ethylpentane	+2.1	+5.3	−2.7	+3.7	+6.8	−2.9	+2.6	+6.0	−1.9	−0.6	+1.9	−2.0
3,3-dimethylpentane	+2.7	+6.0	−2.7	+3.2	+6.2	−2.9	+0.3	+2.9	−1.9			
2,3-dimethylpentane	+2.2	+5.3	−2.6	+4.5	+7.4	−2.8	+0.7	+3.4	−1.9	+0.4	+3.1	−1.9
2,2,4,4-tetramethylpentane	+4.5	+6.7	−1.5	+5.8	+7.6	−1.6	+2.7	+4.9	−0.9	+3.1	+5.5	−1.0
2,3,3,4-tetramethylpentane	+2.4	+3.5	−0.7	+5.1	+6.1	−0.8						
3,3-diethylpentane	+2.4	+3.5	−0.7	+5.2	+6.2	−0.8	−1.4	−1.4	−0.4	<0.1	+0.5	−0.4

Table III
Comparison of the Shape (trans-decalin and cyclopentane) and Steric Hindrance (br-C_9 and br-C_7) Effects in the Different Polymeric Systems and in Some Small Molecule Systems ($X_{12}s_1^{-1}$ is Obtained from h_∞^E and Equation 2)

	$\Delta X_{12}s_1^{-1}$ (J cm^{-3} Å) =			
	$X_{12}s_1^{-1}$(trans) − $X_{12}s_1^{-1}$(cis)	$X_{12}s_1^{-1}$(c-C_5) − $X_{12}s_1^{-1}$(c-C_6)	$X_{12}s_1^{-1}$-(3,3-$Et_2C_5H_{10}$)^a − $X_{12}s_1^{-1}$-(2,2,4,4-$Me_4C_5H_8$)	$X_{12}s_1^{-1}$-(3-EtC_5H_4)^a − $X_{12}s_1^{-1}$-(2,2-$Me_2C_5H_{10}$)
polymer				
PIB	−1.6	−6.5	−4.8^b	−3.5^d
PBD	−1.6	−4.2	−1.5^b	−1.6
PPmer	−3.0	−6.2	−3.2	−2.3^c
Cop 33% E	−3.2	−4.9	ins	−3.1^{c,e}
PP	−4.1	−5.1	−4.5	−2.6^{c,e}
PBu-1	−4.1	−6.0	−3.9	−2.8^c
Cop 75% E	−5.7	ins in c-C_5	−5.0	−4.7
Cop 63% E	−5.0	−7.9	−6.3	−7.4^e
PDMS	−5.5	−7.1	−2.4^f	−2.7^{c,e}
PS^i		−3.0		
small molecule				
br-C_{16}	−1.7^{g,j}			
2,2-dimethylbutane	−2.6^{g,j}			
3,3-diethylpentane	−2.9^{g,j}	−12.1		
n-C_{16}	−3.6^{g,j}	−6.1	−6.0	−2.8^{i,g}
tridodecylamine				−2.9^{c,d,h}
toluene		−6.5		

[a] The difference is made between a sterically hindered (sh) and a not sterically hindered (nsh) compound. For some polymers, the reference either of the sh or of the nsh compound is changed as indicated in order to tabulate the largest difference. [b] The sh compound is 2,3,3,4-tetramethylpentane instead of 3,3-diethylpentane. [c] The nsh compound is 2,4-dimethylpentane instead of 2,2-dimethylpentane (see text). [d] The sh compound is 2,3-dimethylpentane instead of 3-ethylpentane. [e] The sh compound is 3,3-dimethylpentane instead of 3-ethylpentane. [f] The sh compound is 3,3-diethylpentane instead of 2,3,3,4-tetramethylpentane. [g] From data in ref 24. [h] From data in ref 9. [i] From heats of dilution in ref 21. [j] Unpublished work in Dr. Patterson's lab.

III for the polymeric systems and some small molecule ones. The tabulation indicates a similar magnitude of the exothermic contribution to the heats between the two series of systems.

Comparison with χ_H Measurements. Heats of dilution have been measured[21] for a low molecular weight polystyrene (2100) in c-C_5 and c-C_6 from $\phi_2 = 0$ to 0.6. The $\chi_H(\phi_2)$ obtained from heats of dilution can be compared with that corresponding to $\phi_2 = 0.5$ coming from h_∞^E.

In c-C_5, χ_H is found to be respectively 0.12 and 0.15 for the PS and PIB solutions. For the PS solutions, the $X_{12}s_1^{-1}$ which fit $\chi_H(\phi_2)$ can be calculated, and the difference between c-C_5 and c-C_6 gives $\Delta X_{12}s_1^{-1} = -3.8$ J cm^{-3} Å. This smaller value may be caused by the small flexibility of the PS chain or by the presence of the benzene ring. H_M^E diminishes by only 140 J mol^{-1} between c-C_5 and c-C_6; i.e., $\Delta X_{12}s_1^{-1}$ is smaller when the second component is benzene.

Comparison with Free-Energy Measurements. Intrinsic viscosities have been measured in c-C_5 and c-C_6 for the three copolymers[10] and for some homopolymers. c-C_5 has been found to be a much better solvent than the other c-C_n's. Although there must be a negative contribution to the entropy coming from the c-C_5 effect, this means that the enthalpic term is more negative and therefore the net result is a lowering of the free energy. The effect is quite spectacular since, in some systems, the intrinsic viscosity is higher by 20% in c-C_5 than in c-C_6.[10] Furthermore, c-C_5 is the best solvent (of about thirty non-polar solvents) of these copolymers, although the nonfavorable free-volume term is relatively large.

By comparing data either on Figure 1 or on Figure 3, it can be seen that the $X_{12}s_1^{-1}$ values are usually higher for c-C_6 than for the other linear or branched alkanes. This may be due in part to the higher cohesive energy or solubility parameter of c-C_6. However, this larger positive contribution to the heats does not prevent c-C_6 from being a much better solvent for the polyolefines than are the branched alkanes[10] with the same free volume. The mixing with c-C_6 must then bring a larger combinatorial or noncombinatorial entropy of mixing.

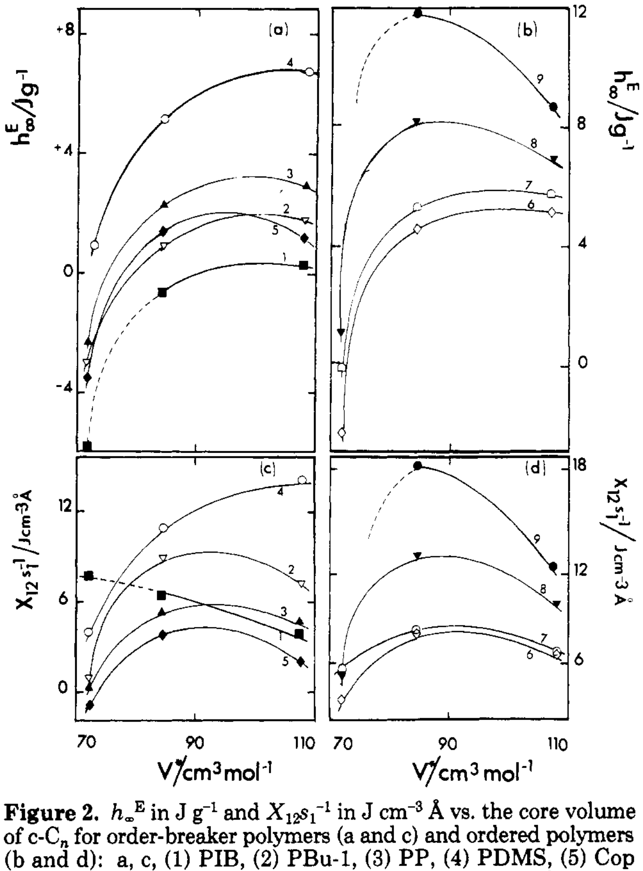

Figure 2. h_∞^E in J g^{-1} and $X_{12}s_1^{-1}$ in J cm^{-3} Å vs. the core volume of c-C_n for order-breaker polymers (a and c) and ordered polymers (b and d): a, c, (1) PIB, (2) PBu-1, (3) PP, (4) PDMS, (5) Cop 33% E; b, d, (6) PPmer, (7) PBD, (8) Cop 63% E, (9) Cop 75% E.

***cis*- and *trans*-Decalin.** The cis and trans isomers of decalin are examples of molecules composed of similar

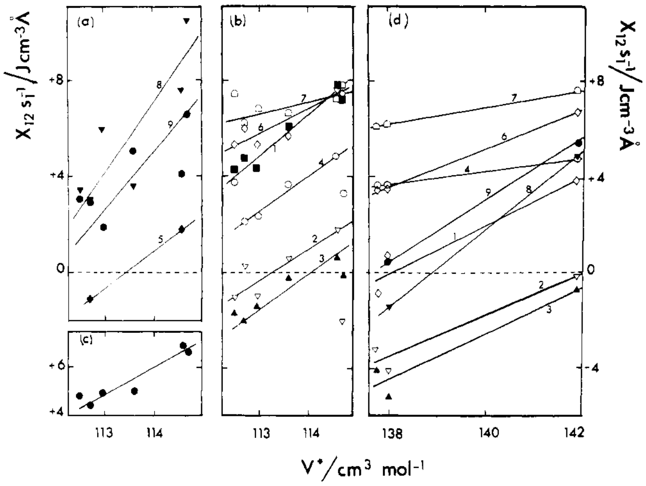

Figure 3. $X_{12}s_1^{-1}$ in J cm^{-3} Å vs. the core volume of the branched heptanes (a for the copolymers, b for the homopolymers, and c for n-C$_{16}$) and that of the branched nonanes (d for all the polymers except Cop 33% E): a, b, d, (1) PIB, (2) PBu-1, (3) PP, (4) PDMS, (5) Cop 33% E, (6) PPmer, (7) PBD, (8) Cop 63% E, (9) Cop 75% E.

groups which have quite different shapes. Heats of mixing have been measured using the cycloalkanes,[17-22] substituted cycloalkanes,[21] and the linear and branched alkanes as the second component.[24] As a spectacular example of the effect of molecular shape on the heats of mixing, one can give H_M^E(*cis*-decalin + c-C$_5$) = −120 J mol^{-1} while H_M^E(*trans*-decalin + c-C$_5$) = −271 J mol^{-1}. These large negative heats do not occur with many systems, but it seems that lower values of H_M^E with the trans isomer are generally obtained in small molecule mixtures. For instance,[14] H_M^E(n-C$_{16}$ + *trans*-decalin) = 76 J mol^{-1} while it would be expected to be around 300 J mol^{-1} because of the positive disordering contribution to the heats. The results can be interpreted by the presence of a negative contribution to the heats in the case of the trans isomer. The magnitude of the negative contribution and of the difference between cis and trans seems to be associated with the anisotropy of the second component. In the small molecule part of Table III, values of $\Delta X_{12}s_1^{-1}$(trans) − $X_{12}s_1^{-1}$(cis) have been listed and are seen to increase with the anisotropy of the second component. The molecular anisotropy, γ^2, of the pure component can be measured by Rayleigh scattering[7] on a pure component and on solutions. The molecular origin of the negative heat is believed to be of a similar nature to that occurring in the sterically hindered alkanes or in c-C$_5$.

The polymer molecules being anisotropic, one would expect a rather large *trans*-decalin effect, i.e., a sizable difference between h_∞^E(trans) and h_∞^E(cis) and possibly negative h_∞^E(trans). In Figure 1, $X_{12}s_1^{-1}$ for *cis-* (□) and *trans-* (■) decalin are far apart, and $X_{12}s_1^{-1}$ is indeed negative for all the polymers except for those where a positive contribution to X_{12} prevails due to a force-field difference contribution (PDMS, PBD, and PPmer) and/or to some disordering in solution (copolymers, PBD, PPmer). The first column of the polymer part of Table III gives the $\Delta X_{12}s_1^{-1}$ for the polymers according to the increasing value of the *trans*-decalin effect.

Anisotropy of a polymer chain is not easy to evaluate quantitatively but must be related to the anisotropy of the segment and also to the way the segments are linked in the chain. The very rigid PIB and more flexible PDMS take the extreme values of $X_{12}s_1^{-1}$, suggesting the importance of the chain flexibility of the second component. PBD and PPmer which have a double bond for every four and every five carbons, respectively, have undoubtedly higher rigidity and consequently lower $\Delta X_{12}s_1^{-1}$ than the saturated polymers. In some cases, when the polymer segment and the small molecule have about the same shape, their $\Delta X_{12}s_1^{-1}$ compare well. This is the case for br-C$_{16}$ and PIB both consisting of highly sterically hindered segments and for the 33% E and 75% E copolymers whose $\Delta X_{12}s_1^{-1}$ is near that of the n-alkanes.

One could expect the trans isomer to be a better solvent than the cis for all the polymers since the heats are much more negative. In most cases, this is indeed the case except for Cop 33% E which is much more expanded in *cis*-decalin (($[\eta]_{\text{cis}} - [\eta]_{\text{trans}})/{}^1/_2([\eta]_{\text{cis}} + [\eta]_{\text{trans}}$) = 28%). This indicates that the excess entropy is larger in *cis*-decalin solutions than in *trans*-decalin solutions for Cop 33% E.

Branched Heptanes and Branched Nonanes of Different Steric Hindrance. Steric hindrance within the molecule has a marked effect on the macroscopic properties of the liquid, particularly in the equation of state quantities such as the molar volume and the thermal expansion coefficient. One expression of this is the conformational rule which states that the isomer with the highest enthalpy also has the lowest molar volume, i.e., steric hindrance lowers the stability of the molecule while increasing the enthalpy. It also decreases the molar volume. This suggests that the molar volume is indicative of the degree of steric hindrance in the isomer. Accordingly, in ref 7 the H_M^E of a series of branched nonanes with n-C$_{16}$ have been plotted against the core volume of the nonanes and found to give a good correlation. From the less sterically hindered 2,2,5-trimethylhexane (V^* = 182.4 cm^3 mol^{-1}) to the more sterically hindered DEP (V^* = 171.0 cm^3 mol^{-1}), H_M^E diminishes from 316 to 18 J mol^{-1}. These results were interpreted as indicative of the existence of a negative steric hindrance contribution which would almost totally compensate for the positive contribution due to the disordering of n-C$_{16}$. With DEP, the steric hindrance contribution would be of the order of −300 J mol^{-1}. A similar correlation has been made[9] with other sterically hindered compounds, the branched heptanes, and another long-chain compound, tridodecylamine.

In Figure 3, the $X_{12}s_1^{-1}$ parameter of the polymers has been plotted against the core volume of the solvent; Figure 3a,b corresponds to the br-C$_7$ with the copolymers and the homopolymers respectively and Figure 3d corresponds to the br-C$_9$ with all the polymers. A correlation of $X_{12}s_1^{-1}$ with the core volume of the solvent is apparent, X_{12} being less positive or more negative with the sterically hindered compounds having a low core volume. In Figure 3c, the $X_{12}s_1^{-1}$ data for the n-C$_{16}$ + br-C$_7$ systems have been plotted.[25] A characteristic feature, namely a X_{12} value lower for 3,3-dimethylpentane than for 2,3-dimethylpentane (although the reverse would be expected from their V^* relative values), is common to the polymeric and nonpolymeric systems. In comparing the $X_{12}s_1^{-1}$ values in the n-C$_{16}$ and in the polymers, it is interesting to find that the variations of $X_{12}s_1^{-1}$ obtained here with the dimethylpentanes follow closely those discovered in n-C$_{16}$ mixtures with the dimethylheptanes (not measured in this work) such as 2,2-dimethyl-, 2,3-dimethyl-, and 2,4-dimethylheptanes.

A similar correlation with V^* can be seen in Figure 3d with the branched nonanes. The steric hindrance contribution to X_{12} can be estimated by the difference between the X_{12} value for a sterically hindered compound and a little or no sterically hindered one. For br-C$_7$'s and br-C$_9$'s, the differences $\Delta X_{12}s_1^{-1}$ = $X_{12}s_1^{-1}$(3,3-dimethylpentane) − $X_{12}s_1^{-1}$(2,4-dimethylpentane) and $X_{12}s_1^{-1}$(3,3-diethyl-

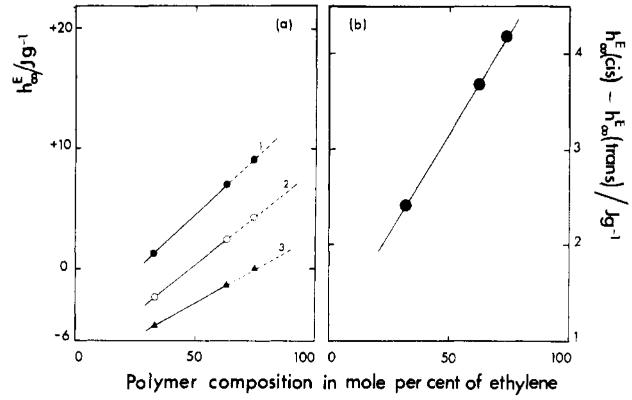

Figure 4. (a) h_∞^E for the copolymers vs. the polymer composition in mole percent of ethylene in c-C_6 (1), *cis*-decalin (2), and *trans*-decalin (3). h_∞^E for the 75% E sample is found by a linear extrapolation of the values for cop 33% E and cop 63% E. The difference between the experimental h^E and the extrapolated value is the heat of fusion of the 75% E sample (17 J g^{-1}). (b) The difference between h_∞^E(cis) – h_∞^E(trans) vs. the polymer composition in mole percent of ethylene. Since this difference is a linear function of the composition and independent of some amount of crystallinity, it can be used as a calorimetric determination of the copolymer composition.

pentane) – $X_{12}s_1^{-1}$(2,2,4,4-tetramethylpentane) have been listed in the third and fourth column of Table III. In some instances, the largest $\Delta X_{12}s_1^{-1}$ was obtained with other substituents as noted in Table III. In a mixture of a branched polymer with a branched solvent, specific shape effects may occur so that the influence of other effects such as the flexibility may be masked. One cannot see a definite trend in the magnitude of the steric hindrance effect except that the branched nonanes are more sterically hindered than the branched heptanes and that the copolymers have higher values of $\Delta X_{12}s_1^{-1}$ than the homopolymers. Polymeric and small molecule second components appear to give $\Delta X_{12}s_1^{-1}$ of similar magnitude.

If the experimental h_∞^E were plotted against V^*, the slope of the line would be somewhat smaller because part of the $X_{12}s_1^{-1}$ variation with V^* comes from the value of $h_{\text{f.v.}}^E$ which increases when the steric hindrance increases.

Specific Interactions between a Branched Polymer and a Branched Solvent. The atactic polyolefins chosen as order breakers in part 1 were used in this steric hindrance investigation because they dissolve easily in hydrocarbons and have themselves different degrees of flexibility and steric hindrance. However, the interpretation of the heats may be less clear with a branched second component than with a linear one due to the possibility of specific interaction associated with the particularly good or bad fitting of the pending groups on the polymer and the solvent. An example of this is the system PBu-1 with 2,2-dimethylpentane which has a very negative heat (–4.0 J g^{-1}), although a value nearer that of the 2,4-dimethylpentane (–2.3 J g^{-1}) would have been expected. It is possible that the three methyl groups at one extremity of the molecule fit well between two ethyl groups of the polymer, so that the usual positive contribution which comes from the mixing of unlike segments has been lowered. This effect is seen but is less pronounced with two other branched polymers, PDMS and PP, where similar interactions are possible. The h_∞^E for the copolymers and the linear polymers seem to show a more regular correlation with V^*.

Heat of Fusion of the 75% Sample. The physical aspect of this polymer, harder and less rubbery than the others, is indicative of the presence of some amount of crystallinity. The large h_∞^E are then the sum of the heat of fusion and the heat of mixing. It was found impossible to measure with a standard DTA apparatus (Perkin-Elmer DSC-1B) the heat of fusion of the pure copolymer. Since measurements of heats of comparable magnitude were made without difficulty on another crystalline polyolefin, poly(4-methylpentene-1), it was thought, in the case of the 75% E copolymer, that the heat was evolved over a large temperature interval. However, the heat of fusion may be obtained indirectly because two noncrystalline copolymers are available. In Figure 4a, values of h_∞^E are plotted vs. the polymer composition for the 33% E and 63% E samples in three solvents, *cis*- and *trans*-decalin and c-C_8. If the solvent has a different heat of mixing for the ethylene and propylene parts, the experimental heat may be a linear function of the composition. The values of h_∞^E extrapolated for the 75% E sample are found to be respectively 4, 3, 0.0, and 9.2 J g^{-1}. These values deducted from the experimental heats 21.0, 16.8, and 25.6 J g^{-1} lead to heats of fusion of 16.7, 16.8, and 16.4 J g^{-1}. The value 17.0 has been used to obtain h_∞^E (Table III) from the experimental heats in the case of the 75% E sample.

Calorimetric Dosage of the Ethylene Content of the Copolymers. Due to the possibility of a slight amount of crystallinity in the ethylene-rich copolymers and not in the others, heats in one solvent cannot be used for accurate composition determination. However, the difference of heats between two solvents is independent of crystallinity and may be a regular function of composition on some concentration range. In Figure 4b, a linear dependence of Δh_∞^E on composition can be seen with the *cis*- and *trans*-decalin systems so that these measurements could be used as an analytical technique. Δh_∞^E extrapolates to 1 J g^{-1} for pure PP although the experimental value is 2.9. This may be caused either by a failure of linearity at the extreme compositions or by a large difference in molecular weight between pure PP (6000) and the copolymers (170 000).

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ESCA and Mass Spectroscopic Studies of Degradations of Poly[bis(trifluoroethoxy)phosphazene]: Pyrolysis, Ultraviolet Light, and Electron Beam Induced Degradations

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Received September 18, 1978

ABSTRACT: Pyrolysis, UV light, and electron beam induced degradations of poly[bis(trifluoroethoxy)phosphazene] have been studied with ESCA and infrared and mass spectroscopic techniques together with gas chromatographic separation. The data obtained reveal the structural changes taking place in the polymer backbone due to the cross-linkage and the oxygen shift to the nitrogen upon the side group elimination. These studies support the mass spectroscopic data of the gaseous products formed in the side group removal.

Polyphosphazenes, polymers having repeating nitrogen–phosphor linkages as backbone chains, are recently gathering renewed interest because of their specific characteristics as processing materials.[1] Allcock and his co-workers reported UV light induced degradation of poly[bis(trifluoroethoxy)phosphazene] under vacuum, along with other polymeric and cyclic oligomer phosphazenes;[2] there they have found gaseous products such as trifluoromethane, 1,1,1-trifluoroethane, and carbon dioxide after a long irradiation at 254 nm. Although some molecular weight changes were observed after irradiation in air, there is no information available about the changes in the backbone. Mochel and Cheng reported a ^{13}C-NMR study of thermal rearrangement of poly[bis(methoxy)phosphazene] up to 150 °C, which involved migration of a methyl group from the methoxy position to the nitrogen.[3] No gaseous products were reported, but some cross-linking was inferred from increase of line widths.

We wish to report here our study of degradations of poly[bis(trifluoroethoxy)phosphazene] in pyrolysis, UV light, and electron beam exposures with ESCA, infrared, and mass spectroscopic techniques together with gas chromatographic product separation.

Our result on the gaseous products formed in the degradation agrees with the reported one.[2] We also observed significant oligomerizations of the high molecular weight polymer, particularly in pyrolysis. The most significant change is the one in the main chain, as revealed in ESCA data of the degradated polymer samples.

Experimental Section

Poly[bis(trifluoroethoxy)phosphazene]. The polymer was prepared from sodium trifluoroethoxide and poly(dichlorophosphazene) in tetrahydrofuran in the same way as reported by Allcock and his co-workers.[4] Its purification was carried out by several precipitations from acetone into water and finally a precipitation from acetone into benzene. The result of its elementary analyses is as follows[5] (the data in parentheses were calculated from the structure): C, 20.30 (19.6); H, 1.66 (1.6); N, 5.86 (5.7); P, 12.00 (12.6); Cl, 0. The fluorine and oxygen analyses were not carried out because of interference by the phosphorus present.[5]

A wide-band ESCA spectrum of the poly[bis(trifluoroethoxy)phosphazene] used in the study reveals the expected amounts of fluorine and oxygen in the sample, as shown in Figure 1. All major peaks of Figure 1 have been assigned to the elements present in the sample. No chlorine was detected at its binding energy of 200 eV even after the data accumulation of 120 time scans.

The purified white powder obtained was dissolved in methyl ethyl ketone, and the polymer films were spin-coated on either aluminum wafers for ESCA and mass spectroscopic studies under electron beams or on sodium chloride plates for infrared absorption studies in pyrolysis and UV light irradiations. The polymer films were then baked under vacuum at 80 °C for a few hours in order to remove any trace of the residual solvent.

Pyrolysis, UV Light, and Electron Beam Exposures. The pyrolysis was conducted under vacuum in a Pyrex glass tube with a break seal; after pyrolysis, the gaseous products were separated with a gas chromatograph with an 8-ft silica gel column at room temperature. Each peak was identified by its mass spectrum and retention time in the column in comparison with those of the authentic samples, trifluoromethane and 1,1,1-trifluoroethane (supplied by PCR Inc.).

The UV light exposures were carried out under vacuum with a Hanovia medium pressure mercury lamp with quartz windows. The gaseous products were analyzed in the same way as in the pyrolysis.

The electron beam exposures were conducted with a Varian scanning Auger gun at 3 KeV electron energy; the estimated dosage was 10^{-4} C/cm^2. The mass spectra of the gaseous products generated during the electron beam exposures were taken simultaneously with the exposures in a typical pressure range of 10^{-4} Pa; the equipment used was described previously.[6]

Analytical Instruments. ESCA measurements were carried out at room temperature under a vacuum better than 3×10^{-7} Pa with a Hewlett-Packard Model 5650B ESCA spectrometer, which had resolution better than 1 eV. The samples were flooded with thermal electrons during the data collections to neutralize the charge effect. The reported binding energies were referred to Au$_{4f7/2}$ transition at 83.9 eV.

[‡] Deceased in 1978.

0024-9297/79/2212-0753$01.00/0