ESR Studies of Polymer Transitions. 2. Activation Volumes of Macromolecules at T_g and $T < T_g$ Relaxations

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ABSTRACT: An independent method is needed to understand the tumbling behaviors of nitroxide probes in ESR studies of polymer relaxations and transitions as a function of probe size. Following a method used by Eby, activation volumes, $\Delta V^{\ddagger}$, in cm^3 mol^{-1} at T_g have been calculated for ten amorphous polymers from isothermal compressibilities, κ_l, and apparent enthalpies of activation, ΔH_a. Log $\Delta V^{\ddagger}$ increases linearly with T_g. $\Delta V^{\ddagger}$ has likewise been calculated for four crystalline and five amorphous polymers at $T < T_g$ (the β relaxation) for both main chains and side chain motion. Values of $\Delta V^{\ddagger}$ at $T < T_g$ are consistently smaller than at T_g and do not vary systematically with T_g or $T < T_g$. The behavior of a series of nitroxide free radical probes used to study relaxation processes by ESR is generally consistent with $\Delta V^{\ddagger}$ values when the temperature of extrema narrowing is compared with estimated diameters of probes.

Recent inquiries into the use of nitroxide free radical probes in ESR experiments for the purpose of studying molecular motion[2-5] both at T_g and also at $T < T_g$ relaxations as a function of probe size[3,5] have emphasized the need for an independent estimate of the molecular volumes involved at T_g and $T < T_g$ relaxations. Relaxation volumes, $\Delta V^{\ddagger}$, calculated by Eby[6] at T_g and $T < T_g$ for a limited series of amorphous and semicrystalline polymers showed two characteristic features which were qualitatively consistent with preliminary studies of probe size: (a) $\Delta V^{\ddagger}$'s at T_g increase rapidly with T_g; (b) $\Delta V^{\ddagger}$'s at $T < T_g$ are smaller and much less dependent on T_g than are $\Delta V^{\ddagger}$'s at T_g.

It was, therefore, decided to extend and revise (where necessary) the early tabulation by Eby. The several quantities to be employed are defined in Figure 1a–d. Figure 1a is part of a dynamic mechanical loss curve, such as is obtained on a torsion pendulum at a frequency of ~1 Hz, in the region of the glass temperature, T_g, and the secondary relaxation at $T < T_g$, frequently designated as T_β for amorphous polymers. Examples of these two loss peaks for many polymers are found in McCrum et al.[7] A detailed discussion of the relationship between $T < T_g$ and T_g has recently been presented.[8]

Figure 1b is a schematic plot of isothermal compressibility, κ, defined as

$$\kappa(\text{atm}^{-1}) = (1/V)\,(\mathrm{d}V/\mathrm{d}P)_T \qquad (1)$$

where V is volume and P is hydrostatic pressure. Such plots for both $T < T_g$ and T_g are rare but have been presented by Heydemann and Guicking[9] for PVC and PMMA. Quach and Simha[10] have made similar measurements for PS and poly(o-methylstyrene). We assume that curves of similar shape will be found for most amorphous polymers.

Figure 1c illustrates the decrease in extrema separation (see Figure 1 of ref 11) of the three-line ESR signal.[2-5,11,12] An extrema separation of 65 G means that the probe is immobile; a separation of 35 G implies considerable mobility. The temperature at which the extrema separation is 50 G (and frequency ~10^7 Hz) is taken as a characteristic temperature, T_{50G}, to correlate with T_g and $T < T_g$. The terms "small probe" and "large probe" refer to molecular volumes of the probe molecules relative to some characteristic molecular parameter of a given polymer. Gross[13] has shown examples for PET. Since the effective frequency of the probe at a line width of about 50 G is about 10^7 Hz, the line narrowing which responds to either a $T < T_g$ or a T_g relaxation occurs at a higher temperature as indicated.

Finally, Figure 1d is a schematic relaxation map showing the frequency variation of a T_g and a $T < T_g$ relaxation with an assumed linearity between 1 and 10^7 Hz. The apparent enthalpies of activation, ΔH_a, are calculated from the slopes of these Arrhenius plots, with the value of ΔH_a at T_g always being greater than that at $T < T_g$.

Figure 2 illustrates the nitroxide probes used in our studies. Probe F was used to obtain a correlation between T_{50G} and T_g.[2-4] The behavior of these probes in six different polymers is discussed elsewhere.[5] All probes shown were obtained from Eastman Kodak, except for F which was obtained from Dr. G. Rabold of the Dow Chemical Co., Midland, Mich.

Discussion

Eby[6] employed a semiempirical relationship for the activation volume $\Delta V^{\ddagger}$ in cm^3 mol^{-1}:

$$\Delta V^{\ddagger} = 4\kappa_l \Delta H_a \qquad (2)$$

where κ_l is defined in Figure 1b and ΔH_a is derived from Figure 1d. Eby described the historical background for this relationship. He tabulated values of $\Delta V^{\ddagger}$ for both amorphous and crystalline polymers. We report $\Delta V^{\ddagger}$ at T_g only for amorphous polymers because of the effects of crystallinity on κ and on T_g. Because effects of crystallinity are not as great at $T < T_g$, values of $\Delta V^{\ddagger}$ will be given for both amorphous and semicrystalline polymers.

Table I is a compilation of κ, ΔH_a, and $\Delta V^{\ddagger}$ values for polymers ranging in T_g values from 148 K for PDMS to 480 K for P(2,6-DMPO). Values of $\Delta V^{\ddagger}$ calculated by Eby are included with a revised value for PMMA. Figure 3 is a semilogarithmic plot of $\Delta V^{\ddagger}$ as a function of T_g. The right-hand ordinate indicates the diameter of a spherical body having the volume shown opposite on the left-hand ordinate.

Referring to values of $\Delta V^{\ddagger}$ from Table I, it is apparent that κ_l changes by a factor of 2 for the range of polymers shown. Hence, the large variation in $\Delta V^{\ddagger}$ arises mainly from the almost exponential increase of ΔH_a with T_g.[14]

Table II collects values of $\Delta V^{\ddagger}$ at $T < T_g$. It has been subdivided into three sections depending on the type of motion involved. This distinction is quite important.[8] In polymers such as PVC, the motion at $T < T_g$ is similar to that at T_g but involves fewer monomer groups. For PET and PC, small moieties between large aromatic groups are moving. For P4MP-1, side group motion is involved. The value of κ is that labeled κ_g in Figure 1b.

There is no simple relationship between $\Delta V^{\ddagger}$ and $T < T_g$ such as that seen in Table I and Figure 1 at T_g. Values for $\Delta V^{\ddagger}$ in groups B and C are consistently smaller than in group A.

Table I
Activation Volumes, $\Delta V^{\ddagger}$, for the Glass Transition, T_g[a]

Polymer	T_g, K	$\Delta H^{\ddagger}{}_a$,[b] kcal mol^{-1}	κ_l, atm^{-1} × 10^5 [c]	$\Delta V^{\ddagger}$, cm^3 mol^{-1}	T, °K	Ref[d]
1. Polydimethylsiloxane	148	20[e]	10.6[f]		303	*e, f*
			12.1[f]		324	
			4	132	T_g	
2. Polyisobutylene	203			127	T_g	*a*
3. Hevea rubber (*cis*-polyisoprene)	203	30	5.1	252	298	*g*
			3.1	154	T_g	
4. Acrylonitrile co (60% butadiene)	233			302	T_g	*a*
5. Poly(vinyl acetate)	300	44	4.7	341	T_g	*h*
6. Poly(vinyl chloride)	343	70	4.4	508	T_g	*i*
7. Atactic polystyrene	373			836	T_g	*a*
8. Poly(methyl methacrylate)	378			1427	T_g	*a*
		100	5.1	845	T_g	*i*
9. Polydiancarbonate	418	150[j]	6.5[j]	1608	T_g	*j*
10. Poly(2,6-dimethylphenylene oxide)	480–498	200[k]	6	1980	T_g	*k, l*

[a] Based on eq 1 according to the method used by Eby;[6] we have accepted Eby's values of $\Delta V^{\ddagger}$ except for PMMA where the value was seemingly too high. If values of ΔH_a and κ_l are missing, $\Delta V^{\ddagger}$ is taken from ref 6. [b] Enthalpy of activation taken from the table in R. F. Boyer, *Rubber Chem. Technol.*, **36,** 1303 (1963), Table XIV, p 1368, except where noted. [c] Coefficient of compressibility in the liquid state just above T_g as in Figure 1b or at a higher temperature as noted in column 6. [d] Reference is to source of $\Delta H^{\ddagger}$ and κ_l in that order. [e] J. M. Pochan, C. L. Beatty, D. D. Hinman, and F. E. Karasz, *J. Polym. Sci., Polym. Phys. Ed.*, **13,** 977 (1975). [f] A. Wiessler, *J. Am. Chem. Soc.*, **71,** 93 (1949). This reference was furnished us by Professor J. Sauer, Rutgers University. The value of κ_l at T_g was obtained by a linear extrapolation of log κ_l against T, a device used for polystyrene by Gee [*Polymer*, **7,** 177 (1966)] in treating the Tait parameter. [g] Value κ_l estimated from a logarithmic decrease with T as in *f*. [h] U. Bianchi, A. Turturro, and G. Basile, *J. Phys. Chem.*, **71,** 3555 (1967). [i] P. Heydemann and H. D. Guicking, *Kolloid Z. Z. Polym.*, **193,** 16 (1964). [j] S. Matsuoka and Y. Ishida, *J. Polym. Sci., Part C*, **14,** 247 (1966). [k] A. V. Savolainen, *Makromol. Chem.*, **172,** 213 (1973). ΔH_a increases to 500 kcal for annealed samples which gives a $\Delta V^{\ddagger}$ of 4950 cm^3 mol^{-1}. [l] We have not located a value of κ_l for this polymer but have assumed the value shown as being similar to the one for polycarbonate. Values of T_g in the literature range from 480 to 498.

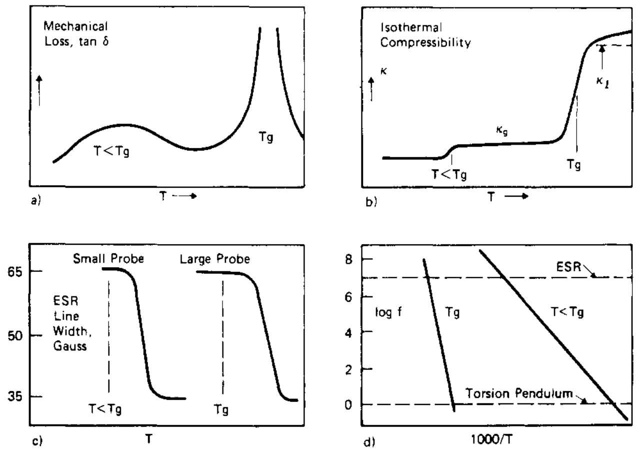

Figure 1. Schematic illustrations of the quantities used in this paper. (a) Dynamic mechanical loss spectrum as a function of temperature in the region of T_g and $T < T_g$; (b) isothermal compressibility at T_g and $T < T_g$; (c) decrease in ESR extrema separation for two different sizes of nitroxide probes; (d) relaxation map for T_g and $T < T_g$ relaxations. ESR has an effective frequency of 10^7 Hz at T_{50G} while the torsion pendulum has a frequency of ~1 Hz.

The subgroup or local mode motion at $T < T_g$ involves one or two monomer units with the main barrier to motion being intramolecular, according to Heijboer.[15] Motion at T_g involves a larger number of monomer units along a given chain as well as some kind of intermolecular interaction. It is to be expected then that $\Delta V^{\ddagger}$ at $T < T_g$ should be less than at T_g. Eby's results suggest that 16 to 29 monomers are moving at T_g in contrast to 2 to 5 at $T < T_g$. Preliminary results indicate that small probes such as A and B are responding to secondary relaxations of small $\Delta V^{\ddagger}$.

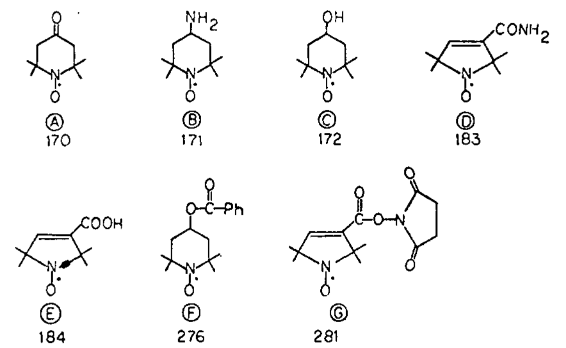

Figure 2. Nitroxide probes used in a study of probe sizes[5] and discussed in this paper in a preliminary fashion. In the sense of Figure 1c, probes A, B, and C are small, and probes F and G are large. These probes give a three-line signal. Molecular weights of probes are given.

Based on eq 2, $\Delta V^{\ddagger}$ for $T < T_g$ must be numerically less than the same quantity at T_g because of the following facts: (a) κ_g = (40–80%) of κ_l; (b) $\Delta H_a(T < T_g) < \Delta H_a(T_g)$ for $T_g <$ 0 °C; (c) $\Delta H_a(T < T_g) \ll \Delta H_a(T_g)$ for $T_g >$ 100 °C. (a) is verified by comparing values of κ_l and κ_g from Tables I and II. (b) and (c) are found in ref 14. Heijboer[11] has suggested a linear relationship between ΔH_a and $T < T_g$ which seems to hold over a wide range of values of $T < T_g$, namely, for $T < T_g$ in degrees Kelvin

$$\Delta H_a = 0.060(T < T_g) \qquad (3)$$

for a frequency of 1 Hz. Since $T < T_g = 0.75T_g$,[8] eq 3 is consistent with the linear plot of ΔH_a against T_g seen in Figure 32 of ref 14.

Table II
Activation Volumes, $\Delta V^{\ddagger}$, for Secondary or $T < T_g$ Relaxation

Polymer	T_g,[a] K	$T < T_g$,[b] °K	$\Delta H^{\ddagger}{}_{(T<T_g)}$,[a] kcal mol^{-1}	κ_g,[d] atm^{-1} × 10^5	$\Delta V^{\ddagger}$, cm^3 mol^{-1}
		(A) Main Chain Motion Same as at T_g			
PTFE	?	160 (1 Hz)			102[e]
PVAc	298	193 (100 Hz)	11[f]	3.6[g]	63
PClTFE	323	253 (11 Hz)	17		63[e]
PVC	343	233 (10^{-4} Hz)	20	3.6[g]	119
PS	373	255 (10^{-4} Hz)	35[h]	3.0[i]	173
PMMA	383	318 (1 Hz)	21	3.1[j]	107
P(2,6-DMPO)	207–225	277[k]	18.6[k]	3[l]	99
		(B) Main Chain Motion Different from That at T_g			
PET	338	243 (165 Hz)	11	2.0[m]	36
Polydiancarbonate	423	158 (100 Hz)	7[n]	3[n]	35
		(C) Side Chain Motion			
Poly(4-methyl-1-pentene)	25	−160 (100 Hz)	7.2[o]	2.5[l]	30

[a] Defined in Figure 1a. Values from ref 14 except where noted. [b] Taken generally from ref 7 except where noted. [c] Taken from Table 14 of ref 14 except where noted. [d] Defined in Figure 1b. [e] From Eby, ref 6. [f] Estimated from Figure 9.16 of ref 7. [g] U. Bianchi, A. Turturro, and G. Basile, *J. Phys. Chem.*, **71**, 3555 (1967). [h] K. Illers, *Z. Elektrochem.*, **65**, 679 (1961). [i] K.-H. Hellwege, W. Knappe, and P. Lehmann, *Kolloid Z. Z. Polym.*, **183**, 110 (1962). [j] G. Allen, D. Sims, and G. J. Wilson, *Polymer*, **2**, 375 (1961). [k] C. I. Chung and J. A. Sauer, *J. Polym. Sci., Part A-2*, **9**, 1097 (1974). [l] Assumed. [m] Footnote *i*, Figure 12. [n] S. Matsuoka and Y. Ishida, *J. Polym. Sci., Part C*, 247 (1966). [o] Estimated from a plot of various literature data.

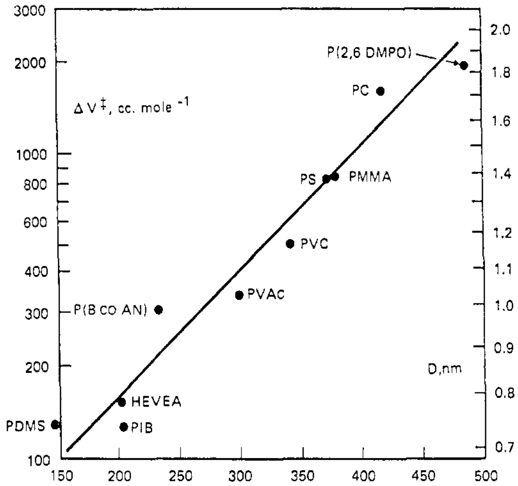

Figure 3. Activation volumes at T_g as a function of T_g, based on the data in Table I. The numbers on the right-hand ordinate are diameters in nm of spherical molecules having the volumes shown opposite on the left-hand ordinate. The numbers on the left ordinate are cm^3 mol^{-1}. Multiplication of nm by ten gives Å.

Use of Activation Volumes in ESR

The smaller the probe size, the lower the temperature at which it starts to tumble in a given polymer.[5,11-13] Rabold[11] found that probe C started to tumble above T_g for PE, PP, and PVC but below T_g for polystyrene. Probe F tumbled above T_g in all four polymers. Probe F was the one he used to make the original correlation between T_{50G} and T_g. We have confirmed his results and further shown that probes F and G tumble at or slightly above T_g in polycarbonate but below T_g in P(2,6-DiCH$_3$PO). Gross[13] showed that probe C tumbled below T_g in PET while a nitro derivative of probe F tumbled at T_g. Savolainen and Törmälä[16] found that probe D was tumbling freely 100 °C below T_g in P(2,6-DiCH$_3$PO). They suggested that it was responding to a $T < T_g$ relaxation. Still other examples are found in ref 12. Size and shape, internal flexibility, and polar interactions of probe with polymer play a role.

Nitroxide probe C in Figure 2 appears to be essentially spherical as judged from two types of molecular models (Dreiding and CPK space filling models) with a diameter of about 8 Å. Probe F has dimensions approximately 8.5 × 8.5 × 13 Å, with some internal flexibility about the ester bond. PVC has a $\Delta V^{\ddagger}$ corresponding to a spherical probe of ~12 Å diameter. Probe C does not start to tumble until above the T_g of PVC but below the T_g of PS which corresponds to 12 Å diameter. Probe F with an isotropic tumbling diameter of about 13 Å responds to T_g in polycarbonate but is tumbling freely below T_g of P(2,6-DCMPO). Thus values of $\Delta V^{\ddagger}$ are reasonably consistent with the rotational behavior of several probes in the indicated polymers.

Kusumoto[17] developed an equation to relate T_{50G} and T_g as follows:

$$T_{50G} - T_g = 52(2.9[\ln(1/f) + 1]f - 1) \tag{4}$$

where $f = V_p/V_s$, V_p being the volume of the probe and V_s being the volume of the polymer segment. This is equivalent to using f as a fitting parameter. We prefer the approach in Figure 3 because values of $\Delta V^{\ddagger}$ are completely independent of ESR data. A better estimate of the applicability of $\Delta V^{\ddagger}$ will be available when probe size studies are completed. For example, all seven probes of Figure 2 are being tested in PIB and PDMS, both low $\Delta V^{\ddagger}$ polymers.

Summary and Conclusions

Following Eby,[6] we have calculated activation volumes, $\Delta V^{\ddagger}$, at T_g by use of eq 2 for a series of atactic polymers ranging from PDMS with T_g = 148 K to PDMPO with a T_g of 478 K. To a good approximation $\Delta V^{\ddagger}$ increases exponentially with T_g, as seen in Figure 3. This is mainly a consequence of the exponential increase in apparent enthalpies of activation with T_g.

Again following Eby, we estimated activation volumes for the glassy state subgroup relaxations arising from in-chain or side-chain motion in both amorphous and semicrystalline polymers. As Eby noted, these values of $\Delta V^{\ddagger}$ are consistently smaller than the ones for T_g in the same polymer. Moreover, there is no systematic variation with $T < T_g$ or with T_g.

The tumbling behavior of nitroxide probes of different sizes, as observed by ESR spectrometry in a limited number of polymers, is qualitatively, and even semiquantitatively, related to $\Delta V^{\ddagger}$. An extensive study of seven probes in six polymers should clarify this subject when completed.

Meanwhile, the correlation shown in Figure 3 is new and may have application in areas other than the ESR work which prompted this study.

References and Notes

(1) (a) Midland Macromolecular Institute; (b) Saginaw Valley State College.

(2) (a) P. L. Kumler and R. F. Boyer, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **16**, 572 (1975); (b) S. Keinath, P. L. Kumler, and R. F. Boyer, *ibid.*, **16**, 120 (1975).

(3) P. L. Kumler, S. Keinath, and R. F. Boyer, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, 17 (**2**), 28 (1976).

(4) P. L. Kumler and R. F. Boyer, *Macromolecules*, **9**, 903 (1976).

(5) P. L. Kumler and R. F. Boyer, probe size studies manuscript in preparation.

(6) R. K. Eby, *J. Chem. Phys.*, **37**, 2785 (1962).

(7) N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids", Wiley, New York, N.Y., 1967.

(8) R. F. Boyer, *J. Polym. Sci., Polym. Symp.*, **No. 50**, 189 (1975), especially pp 195–198 and 212–218.

(9) P. Heydemann and H. D. Guicking, *Kolloid Z. Z. Polym.*, **193**, 16 (1964).

(10) A. Quach and R. Simha, *J. Appl. Phys.*, **42**, 4592 (1971).

(11) G. P. Rabold, *J. Polym. Sci., Part A-1*, **7**, 1203 (1969).

(12) A. L. Buchachenko, A. L. Kovarskii, and A. M. Vasserman, "Advances in Polymer Science", Z. A. Rogovin, Ed., Wiley, New York, N.Y., 1974, pp 26–57.

(13) S. C. Gross, *J. Polym. Sci., Part A-1*, **9**, 3327 (1971).

(14) R. F. Boyer, *Rubber Chem. Technol.*, **46**, 1303 (1963), especially Table XIV, Figures 32, 34, 35, and eq 53–57.

(15) J. Heijboer, Atti del Z° Convegno della Societa de Reologia, Siena, May 10–12, 1973; also Communication No. 508 from TNO, Laboratories, Delft, The Netherlands.

(16) A. Savolainen and P. Törmälä, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1251 (1974).

(17) N. Kusumoto, Preprints ESR Symposium, Matsuyama, Japan 1973. S. N. Kusumoto, S. Sano, N. Zaitsu, and Y. Motozato, *Polymer*, **17**, 448 (1976), for an application of eq 4 to natural rubber and butadiene–acrylonitrile rubber.

Trisubstituted Ethylenes Containing Halo, Cyano, and Carbomethoxy Substituents. New Reactive Comonomers

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Received August 19, 1976

ABSTRACT: New electron-poor trisubstituted olefins were synthesized by dechlorocarbomethoxylation reactions, a Wittig reaction, and substitution of activated chloroolefins by potassium fluoride in the presence of a crown ether. These new monomers, along with several trisubstituted olefins from the literature, copolymerized with electron-rich monosubstituted ethylenes and bicyclobutane monomers under free radical conditions. Charge-transfer complexes of *p*-methoxystyrene were observed with every trisubstituted olefin except **16** and **18**. Spontaneous cationic homopolymerization of *p*-methoxystyrene, caused by several of the electrophilic olefins, occurred simultaneously with their radical-induced copolymerizations, and only dimethyl 2-cyanoethylene-1,1-dicarboxylate gave strictly 1:1 copolymers. 1-Chloro-olefins gave copolymers approaching 1:1 composition whereas 2-chloro- and 2-fluoroolefins were less satisfactory comonomers.

Electron-poor trisubstituted olefins bearing cyano and/or ester substituents are excellent comonomers for electron-rich monosubstituted olefins,[1,2] as well as for bicyclobutane monomers.[3] The adverse steric effect of the 2 substituent is largely counteracted by the two 1 substituents, which strongly stabilize the intermediate electron-poor radical. Moreover, the electron-poor character of these olefins makes them very susceptible to attack by electron-rich radicals. It was of interest to see if the replacement of either cyano or ester group by chloro substituents would still allow them to copolymerize with electron-rich olefins. Early work on the copolymerization of the chloroethylenes with styrene had already shown trichloroethylene to be more reactive than vinyl chloride to the polystyryl radical.[4]

Our purposes in introducing chloro substituents were threefold: (1) ready synthesis of monomers; (2) nonflammability of resulting copolymers, and (3) processability of resulting copolymers. The cyano- and ester-containing monomers synthesized earlier gave copolymers of too high T_g to be processable, and it was thought that substitution of ester or cyano groups by chloro might lead to more tractable materials.

During this study, investigation of one fluorine-containing analogue appeared warranted, as did the synthesis of one new monomer containing only cyano and carbomethoxy groups.

Results

Synthesis and Copolymerization of 1-Chloroolefins 3, 6, and 10. The desired monomers were synthesized from available trisubstituted monomers by our new de(chlorocarbomethoxylation) reaction,[5] demonstrating its generality (Scheme I). (No doubt **3** could also be prepared from dimethyl maleate by chlorination–dehydrochlorination.)

These 1-chloroolefins copolymerized readily with several styrene monomers under free-radical conditions. The copolymers, obtained in 61–80% yields, had inherent viscosities 0.37–0.73 dl g^{-1} and formed fibrous precipitates when their solutions were poured into methanol. The electron-rich comonomers *p*-methoxystyrene and styrene gave approximately 1:1 compositions, while the more electron-poor 2,5-dichlorostyrene incorporated significantly less of the electron-poor olefin. Charge-transfer complexation of *p*-methoxystyrene with the three ethylenes took place as evidenced by the transient formation of bright colors on mixing the ingredients.

Thermal Behavior. The glass transition and thermal decomposition temperatures were determined on a differential scanning calorimeter (Table I). In most cases clearly defined T_g's were visible. These lay between 150 and 225 °C. While high, they were much lower than those noted previously[2] for