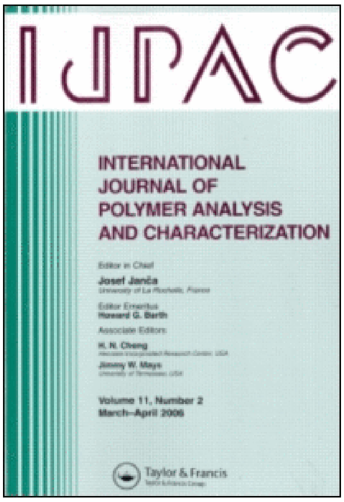

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Use of Paramagnetic Relaxation Agents in the Characterization of Acrylic Polymers: Application of Chromium (III) Acetylacetonate and Iron (III) Acetylacetonate

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Use of Paramagnetic Relaxation Agents in the Characterization of Acrylic Polymers: Application of Chromium (III) Acetylacetonate and Iron (III) Acetylacetonate

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The quantitation of acrylate polymers by high-resolution ^{13}C-NMR requires a knowledge of the spin-lattice relaxation times. For signals from non-protonated carbons, such as carbonyls, these relaxation times are frequently on the order of 1.5–2.0 s. Through the use of paramagnetic relaxation agents, it is possible to decrease the relaxation times. For poly(methyl methacrylate), poly(butyl methacrylate), and poly(hydroxyethyl methacrylate), it has been shown that Cr(acac)$_3$ and Fe(acac)$_3$ can be used to decrease the T_1 of all ^{13}C signals. Guidelines for the use of these relaxation agents in acrylics are given.

KEY WORDS Paramagnetic agents, ^{13}C-NMR, spin lattice, acrylate polymers

INTRODUCTION

Acrylic polymers, such as poly(methyl methacrylate) (PMMA) and poly(2-hydroxyethyl methacrylate) (PHEMA), are used in the coatings industry as paint vehicles because of their clarity, stability, and chemical inertness. The microstructure of these homopolymers has been studied in some detail using ^{13}C-NMR [1–3]. In addition to the information derived from the chemical shift data, spin lattice relaxation times have also been used to probe structural details of PMMA [1].

A study of the spin-lattice relaxation time T_1 can provide information on chain flexability and mechanisms of relaxation. In addition, knowledge of T_1 is necessary for quantitative determination of composition in mixtures of these polymers. Ideally, when signal-averaging NMR acquisitions using inverse-gated decoupling, each measurement should not be repeated more often than once in ten T_1 intervals.

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Spin lattice relaxation times give the rate of energy transfer from a nuclear spin system to its surroundings and describe the return of the z component of magnetization, M_t, to equilibrium (M_o) after a pulse. Assuming a single exponential return to equilibrium following the 180 - t - 90 pulse sequence, intensity data (I_t) can be fitted to the equation shown below to obtain the value for T_1.

$$I_t = (M_t - M_o) * \exp(-t/T_1) + M_o$$

Spin lattice relaxation can proceed by several mechanisms. The most relevant one for polymer solutions with spin 1/2 nuclei is dipole-dipole interactions which, in the case of ^{13}C, is accomplished by nearby protons. Since the dipole-dipole relaxation depends on the inverse sixth power of the inter-dipole distance, this effect is relatively short range. This leads to longer relaxation times for nonprotonated carbons. Dipole-dipole relaxation can also occur between an unpaired electron and the nucleus of interest. Because the electron-dipole interaction contributes much more towards relaxation than nuclear-dipole, this effect (where present) dominates. This mechanism is of particular interest as it is believed to be the main source of relaxation from paramagnetic relaxation agents.

Paramagnetic relaxation agents are typically coordination complexes of Cr (III), Fe (III), or Gd (III). These complexes contain unpaired electrons which contribute to electron-dipole spin lattice relaxation. One criterion necessary for a useful nonspecific relaxation agent is that it not interact selectively with any portion of the structure of interest. Early reports in the literature indicated that common relaxation agents such as $Cr(acac)_3$ decreased the spin lattice relaxation time without changing the chemical shift [4–7]. However, in recent years, paramagnetic relaxation agents have been shown to interact with aromatic compounds [8–13], hydrogen-bond donors [14, 15] and halogenated solvents [16, 17]. These interactions are seen both as slight perturbations in the chemical shift and in selective relaxation.

In addition to reducing the overall T_1, paramagnetic relaxation agents were originally reported to quench NOE [4, 18–21]. It was reported later that the NOE will not be suppressed universally but only in those systems in which inefficient ^1H–^{13}C dipole-dipole relaxation occurs [16].

The published applications of relaxation agents to polymeric systems are relatively few. It is the intention of this work to provide information on the effect of relaxation agents on some acrylate polymers of commercial importance in order to arrive at reasonable guidelines for obtaining quantitative spectra of mixtures or blends of these materials.

EXPERIMENT

Poly(methyl methacrylate) (PMMA), and poly(butyl methacrylate) (PBMA), samples were obtained from Scientific Polymer Products, Inc. (Ontario, NY). Poly(2-hydroxyethyl methacrylate) (PHEMA), $Cr(acac)_3$, tris(acetylacetonato)chromium(III), and $Fe(acac)_3$, tris(acetylacetonato)iron(III), were obtained from Aldrich Chemical Co. (Milwaukee, WI). The characteristics of the polymers used are given in Table I. The two MW grades of PMMA have about the same tacticity distribution: *rr* 52%, *mr* 43%, and *mm* 5.5%. The polymer molecular weight data given in Table I were obtained from the manufacturer, and the tacticity was determined using ^{13}C-NMR.

TABLE I

Polymers Used in this Study.

Polymer	Tacticity	M_n	M_w	Technique
PMMA	syndiotactic	48,300	101,000	GPC
PMMA	syndiotactic		33,000	GPC
PBMA	syndiotactic		100,000	GPC
PHEMA			300,000	Intrinsic Visc.

The two MW grades of PMMA have about the same tacticity distribution: *rr* 52%, *mr* 43%, and *mm* 5.5%.

^{13}C-NMR spectra were obtained at 100.58 MHz on a Varian VXR 400 NMR spectrometer on 20 wt/vol% solutions of the polymers using a 10-mm broadbanded probe. Data were collected using a standard inversion recovery pulse sequence with a spectral width of 35 KHz, an acquisition time of about 1 s or greater, and continuous Waltz decoupling (unless otherwise specified as inverse-gated decoupling, that is, decoupler only on during acquisition). The temperatures were 30°, 18°, and 100°C for PMMA, PBMA, and PHEMA samples, respectively. The 90° pulse ranged from 12–27 μs, depending on the probe and amplifier setting used. For each T_l experiment, 10–12 data points were collected, and 64–96 transients were collected for each data point. For each sample, two data sets were collected, with the transmitter centered either in the carbonyl or in the aliphatic region. Data were processed using an exponential multiplication line-broadening parameter of 10 Hz (3.5 Hz for PBMA data); there was generally little change in the T_l value, but an increase in the accuracy of the fit, going from 3.5 to 10 Hz line-broadening. The recycle delay time was 15 or more times the longest T_l measured in each experiment. Chemical shifts were referenced to the carbon of chloroform-d_l at 77.0 ppm or of DMSO-d_6 at 39.5 ppm.

The T_l experiments were not designed to give optimal accuracy, for example the delay times used were not optimized given the resultant T_l values, and reproducibility studies were not done. However, the data were used to demonstrate the usefulness of relaxation agents for quantitative ^{13}C-NMR measurements in polymers and to provide a guideline in choosing the type and quantity of relaxation agent to use.

RESULTS AND DISCUSSION

The T_l values obtained as a function of the type and amount of relaxation agent used are shown in Tables II–VI. The values for *mm* and end groups resonances have greater error due to the low signal to noise of these resonances. A substantial reduction in T_l values occurs with 0.025 M relaxation agent, and a modest further reduction occurs as the concentration of relaxation agent increases to 0.050 M. The useful concentration limit for Cr(acac)$_3$ has been reported to be 0.1 M in organic solvents [21]. The magnitude of the reduction is more pronounced for carbons with longer T_l values. For PMMA at either molecular weight we observe the changes shown in Table VII. For PMMA with the addition of 0.05M Cr(acac)$_3$, T_l values of about 0.08 s or less are not affected by 0.05 M Cr(acac)$_3$.

In the absence of specific interactions, the T_l observed (T_l^{obsd}) can be related to the T_l^{e} as follows:

TABLE II

T_1 for PMMA (M_w 33,000) in $CDCl_3$.

Assign.	Tacticity	no relax. agent *ppm*	no relax. agent T_1.s	0.025 M $Cr(acac)_3$ T_1.s	0.050 M $Cr(acac)_3$ T_1.s	0.025 M $Fe(acac)_3$ T_1.s	0.050 M $Fe(acac)_3$ T_1.s
C = O	rr	177.89	1.3	0.55	0.34	0.39	0.25
	rr	177.60	1.3	0.55	0.34	0.39	0.25
	mr	176.89	1.3	0.55	0.35	0.38	0.25
	mr	176.73	1.3	0.56	0.35	0.39	0.26
	mm	175.94	1.5	0.56	0.37	0.41	0.29
CH_2		54.24	0.14	0.11	0.10	0.10	0.093
OCH_3		51.61	0.85	0.30	0.19	0.21	0.14
C quat.	mm	45.33	1.9	0.65	0.42	0.45	0.33
	mr	44.68	1.9	0.66	0.40	0.47	0.31
	rr	44.34	1.9	0.65	0.40	0.47	0.31
CH_3	end	29.40	1.3	0.62	0.40	0.45	0.30
CH_3	mm	20.86	0.12	0.10	0.10	0.11	0.089
	mr	18.54	0.11	0.10	0.093	0.094	0.084
	rr	16.25	0.080	0.080	0.076	0.078	0.070

TABLE III

T_1 for PMMA (M_w 33,000) in $CDCl_3$ with inverse-gated decoupling.

Assign.	Tacticity	no relax. agent *ppm*	no relax. agent T_1.s	0.025 M $Cr(acac)_3$ T_1.s	0.050 M $Cr(acac)_3$ T_1.s	0.025 M $Fe(acac)_3$ T_1.s	0.050 M $Fe(acac)_3$ T_1.s
C = O	rr	174.46	1.3	0.56	0.36	0.42	0.23
	rr	177.17	1.3	0.55	0.36	0.43	0.24
	mr	176.48	1.4	0.56	0.38	0.42	0.25
	mr	176.31	1.4	0.56	0.37	0.44	0.25
	mm	175.55	1.6	0.54	0.41	0.49	0.23
CH_2		53.92	0.15	0.12	0.11	0.11	0.091
OCH_3		51.24	1.0	0.33	0.21	0.23	0.13
C quat.	mm	45.00	2.0	0.70	0.43	0.50	0.28
	mr	44.58	1.9	0.68	0.44	0.50	0.28
	rr	44.23	1.8	0.69	0.44	0.50	0.28
CH_3	end	29.21	1.7	0.75	0.36	0.34	0.26
CH_3	mm	20.77	0.15	0.13	0.096	0.11	0.086
	mr	18.43	0.14	0.10	0.092	0.093	0.081
	rr	16.21	0.082	0.085	0.079	0.079	0.067

$$1/T_1^{\text{obsd}} = 1/T_1^{\text{dia}} + 1/T_1^{e}$$

where T_1^{dia} is the T_1 without relaxation agent and $1/T_1^e = R_1^e$ is the rate of relaxation due to the relaxation agent [11]. This will depend on the strength of the electron—nuclear dipole—dipole interaction, which will depend on the concentration and nature of the solute, the concentration and type of relaxation agent, the presence of other solute molecules, the solvent viscosity, temperature and the type of solvent. For each specific combination of these factors, there will be a different minimum T_1 value to which the nuclei are 'leveled'; nuclei with other relaxation mechanisms still competitive with electron—nuclear dipole—dipole interaction may well have T_1 values less than this 'minimum level'.

TABLE IV

T_1 for PMMA (M_w 101,000) in $CDCl_3$.

Assign.	Tacticity	no relax. agent ppm	no relax. agent T_1,s	0.025 M $Cr(acac)_3$ • T_1,s	0.050 M $Cr(acac)_3$ T_1,s	0.025 M $Fe(acac)_3$ T_1,s	0.050 M $Fe(acac)_3$ T_1,s
C = O	rr	177.86	1.2	0.60	0.38	0.46	0.26
	rr	177.58	1.3	0.61	0.38	0.46	0.26
	mr	176.89	1.4	0.63	0.40	0.48	0.26
	mr	176.71	1.3	0.62	0.39	0.47	0.26
	mm	175.94	1.6	0.78	0.38	0.48	0.25
CH_2		54.33	0.12	0.11	0.11	0.10	0.093
OCH_3		51.55	0.81	0.36	0.23	0.22	0.084
C quat.	mm	45.43	2.0	0.79	0.46	0.45	0.29
	mr	44.80	1.9	0.82	0.48	0.50	0.30
	rr	44.46	1.9	0.80	0.47	0.49	0.29
CH_3	end	29.47	2.0	0.99	0.58	0.38	0.29
CH_3	mm	20.98	0.14	0.14	0.12	0.13	0.11
	mr	18.65	0.12	0.10	0.10	0.092	0.086
	rr	16.43	0.096	0.084	0.086	0.077	0.071

TABLE V

T_1 for PBMA in $CDCl_3$.

Assign.	Tacticity	no relax. agent ppm	no relax. agent T_1,s	0.025 M $Cr(acac)_3$ T_1,s	0.050 M $Cr(acac)_3$ T_1,s	0.025 M $Fe(acac)_3$ T_1,s	0.050 M $Fe(acac)_3$ T_1,s
C = O	rr	177.74	1.4	0.84	0.59	0.79	0.41
	rr	177.40	1.4	0.84	0.58	0.78	0.41
	mr	176.84	1.4	0.84	0.57	0.82	0.40
	mr	176.68	1.4	0.80	0.58	0.83	0.42
	mm	175.91	1.2	0.92	–	–	0.49
OCH_2		64.61	0.35	0.29	0.27	0.28	0.20
CH_2		54.54	0.11	0.12	0.12	0.12	0.12
C quat.	mm	45.66	1.9	1.6	–	–	0.61
	mr	45.01	2.0	1.1	0.83	1.0	0.53
	rr	44.64	2.0	1.1	0.82	1.1	0.52
CH_3	mm	–			–	–	–
	mr	18.25	0.90	0.089	0.087	0.089	0.078
	rr	16.37	0.85	0.079	0.080	0.080	0.074
CH_2		30.13	0.57	0.42	0.36	0.40	0.19
		19.24	1.2	0.68	0.53	0.61	0.30
		13.62	2.1	0.86	0.57	0.76	0.33

The reduction in T_1 for PBMA and PHEMA is not as great as for PMMA. This is due partially to the bulkier ester group in these polymers which decreases the complexation constant between the relaxation agent and the polymer. In addition, PHEMA was run at higher temperatures than PMMA. This will decrease the amount of complex formed between the acrylate polymer and the relaxation agent and hence decrease the relaxation agent contribution to the T_1 value measured. It may also be that the solvents $CDCl_3$ and DMSO-d_6 compete more effectively with PBMA and PHEMA, respectively, for outer sphere sites on the relaxation agent than $CDCl_3$ does in the $CDCl_3$-PMMA system.

Use of $Fe(acac)_3$ gives a more pronounced reduction in T_1 values at each concentration than does $Cr(acac)_3$, as has been previously reported [22]. The effect of a particular

TABLE VI

T_l for PHEMA in $CDCl_3$.

Assign.	Tacticity	no relax. agent *ppm*	no relax. agent T_l,s	0.025 M $Cr(acac)_3$ T_l,s	0.050 M $Cr(acac)_3$ T_l,s	0.025 M $Fe(acac)_3$ T_l,s	0.050 M $Fe(acac)_3$ T_l,s
C = O	rr	176.75	1.2	0.57	0.40	0.44	0.32
	rr	176.50	1.2	0.58	0.40	0.43	–
	mr	176.06	1.3	0.57	0.39	0.44	0.32
	mr	175.88	1.3	0.59	0.40	0.42	0.33
	mm	–	–	–	–	–	–
OCH_2-		65.73	0.39	0.25	0.19	0.19	0.16
$-CH_2$-OH		58.35	0.59	0.30	0.21	0.18	0.15
CH_2		52.92	0.11	0.08	0.08	0.10	0.09
C quat.	mm	–	–	–	–	–	–
	mr	44.54	1.92	0.73	0.48	0.53	0.40
	rr	44.19	1.91	0.73	0.48	0.53	0.38
CH_3	end	–	–	–	–	–	–
CH_3	mm	–	–	–	–	–	–
	mr	18.14	0.14	0.11	0.10	0.13	0.12
	rr	16.46	0.14	0.11	0.10	0.12	0.11

TABLE VII

Summary of T_l Reduction due to Relaxation Agents for PMMA.

Original T_l. *s*	T_l With 0.05 M Cr(acac)3 (s)	
0.11	0.1	10–20% reduction
0.85	0.2	reduced factor of ≅4
1.3–1.9	0.35–0.48	reduced factor of ≅4

metal$(acac)_3$ complex depends on the rotational/diffusion motion of that complex, on the metal dipole moment, and on the electron spin relaxation rate. The greater effectiveness of the $Fe(acac)_3$ has been attributed mainly to its larger electron dipole moment [15]. $Fe(acac)_3$ has also been reported to be more soluble than $Cr(acac)_3$ [22]. However, we find that the lock is substantially affected when using $Fe(acac)_3$; the automatic lock and shim features on the Varian spectrometer failed on the 0.05 M $Fe(acac)_3$ sample. $Fe(acac)_3$ has also been reported to be moisture sensitive [8], and to react with CCl_4 [17]. $Cr(acac)_3$ is less chemically reactive [5]. The line widths of the carbon resonances of PMMA were about the same using 0.05 M $Cr(acac)_3$ or 0.05 M $Fe(acac)_3$ (Fig. 1, 2.5 Hz line broadening). However, the line widths of the carbon signals for PHEMA were substantially broadened with the use of $Fe(acac)_3$.

Tables II and III compare the T_l values of PMMA (M_w 33,000) using continuous Waltz decoupling or inverse-gated Waltz decoupling (Waltz decoupling on only during acquisition). The T_l will be nonexponential when inverse gated decoupling is used. The T_l should be shorter when inverse-gated decoupling is used because of the dipolar contribution of the protons to the carbon relaxation. With inverse-gated decoupling, the carbon magnetization will be increased by NOE effects from the protons during the acquisition time. The nonequilibrium effects of this intermittent NOE on the carbon magnetization can require a delay of 10–15 × T_l to dissipate [23], rather than the normal 5 × T_l usually accepted for systems with no proton irradiation or continuous decoupling. As can be seen from data in

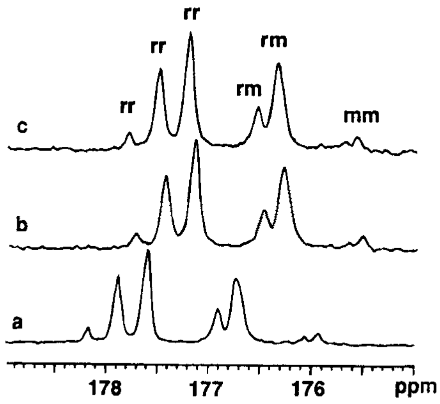

FIGURE 1. ^{13}C-NMR spectra (2.5-Hz line broadening) of the carbonyl region of PMMA with a) no relaxation agent, b) 0.05 M Cr(acac)$_3$, and c) 0.05 M Fe(acac)$_3$.

Tables II and III, T_l values are slightly shorter using inverse-gated decoupling, as expected. We did not observe nonexponential behavior, as our delay times always exceeded 10× T_l. Other workers have also observed that the T_l values are slightly longer when using broad band irradiation *vs.* inverse-gated decoupling and that this effect persists in the presence of relaxation agent [24]. There is some controversy as to whether and how much the NOE effect is quenched in the presence of relaxation agents; however, these shorter relaxation times definitely indicate that proton-carbon dipole interactions are still in effect. The magnitude of NOE effects will depend on the relative magnitude of the proton—carbon dipole—dipole coupling and the nuclear—electron dipole—dipole interaction. This may depend on the molecular weight and segmental motion of the polymer, the strength of the carbon-proton interaction, the rate of spin flips of the specific carbon in the presence of the relaxation agent, and any preferential coordination with the relaxation agent. Further investigations into this effect are in progress.

Carbon T_l values decrease with increasing molecular weight up to about 3,000 g/mol, after which they become relatively independent of molecular weight [25, 26]. This is because the nuclear correlation time is governed predominantly by segmental motions of the polymer chain, and not by the overall correlation time of the polymer molecule. Segmental motion is relatively invariant with increasing molecular weight. In Tables II and IV are listed the T_l values of PMMA of molecular weight 33,000 and 101,000, respectively. The T_l values are approximately the same for either molecular weight in the absence of relaxation agents (the carbonyl carbon T_l values are about the same, the backbone CH_2 and OCH_3 T_l values are slightly shorter, and the α-CH_3 T_l values are slightly longer at higher M_W). In the presence of the relaxation agent, the T_l values are consistently longer for the higher molecular weight material as compared to the lower molecular weight material. This difference is greater at lower concentrations of the relaxation agent. This may be the result of a larger average distance between the polymer nuclei and the relaxation agent for higher molecular weight polymers.

It has been reported that the carbon T_l values are longer in isotactic (*mm*) PMMA than in syndiotactic (*rr*) PMMA [1]. Other researchers have found no effect of tacticity of the carbonyl carbon T_l values in ^{13}C-enriched, predominantly syndiotactic PMMA [2]. For

PMMA, we observe a small increase in T_1 values in the order *rr* < *mr* < *mm* for the α-CH_3, quaternary, and carbonyl carbons. Changes in the T_1 as a function of tacticity could be different due to the stereochemical effects of the sequence on the motion of carbons and/or dipole interactions. Similar effects are seen for the PHEMA carbonyl and quaternary signals, as well as the PBMA α-CH_3. As can be seen most clearly from the α-CH_3 data, the relaxation agent does not change the relative ordering of the T_1 values as a function of tacticity. There is no preferential relaxation with respect to tacticity. Although with less strongly interacting solvents, an effect might be observed.

The T_1 values of carbons in polymers are a function of the correlation time, or the degree of motion, of the particular carbon. Carbons in polymer side chains and end groups generally have longer T_1 values than backbone carbons [27, 28]. Methyl groups in particular have longer T_1 values due to their increased ability to rotate. This trend is readily observed in our data. The T_1 of the end-group methyl resonance is about 10× longer than that of the backbone CH_2 carbons in PMMA, though the error in the end-group measurement is large due to its lower signal to noise. In PBMA the T_1 values of the butyl ester carbons increase as their distance from the polymer backbone increases. The methyl-end carbon of the butyl ester has a T_1 about 7× longer than that of the backbone CH_2 segment. The T_1 values of end group or branch carbons and backbone carbons are much closer in value when a relaxation agent is used. The terminal -CH_2OH in the PHEMA has a longer T_1 value than either the adjacent methylene or backbone signals.

T_1 values in polymer systems generally increase with an increase in temperature. This is due to a decrease in the correlation times of the motions responsible for the relaxation [25]. Thus changes in temperature can lead to a change in the relative strength of the proton—nuclear dipole—dipole interaction and the electron—nuclear dipole interaction of the solute with the relaxation agent. For this reason relaxation agents may be more effective at higher temperatures. This may, however, be offset by the decrease in the specific complexation between the polymer and the relaxation agent.

The chemical shift position of the resonances relative to that of the solvent chloroform is affected by the relaxation agent, as is demonstrated in Figure 1. This is also illustrated in Table VIII with the data for PMMA (M_W 33,000) and in Table IX for PHEMA which is discussed below. The carbonyl carbon resonances in PMMA are shifted slightly more than, for example, the α-methyl resonances. This suggests that the carbonyl group may be complexed with the relaxation agent. The shifts we observe are predominately due to the solvent resonance as chloroform has been reported to have strong interactions with $Cr(acac)_3$ [16].

Any interaction of either the substrate molecule or the solvent with the relaxation agent can alter the strength of the electron-nuclear dipole interaction, which will be seen in the T_1 determination. Interactions with the solvent would result in an increase in the average distance between the relaxation agent and the substrate. This should be shown as an increase in the T_1 with a relaxation agent over the T_1 measured in a noninteracting solvent. Another indication of interaction between the substrate and the relaxation agent will be seen in a change in the chemical shift. Chlorinated solvents have been shown to interact with $Cr(acac)_3$ [17]. Tables VIII and IX show the effect on the chemical shift of PMMA and PHEMA upon the addition of relaxation agents. A small but significant upfield shift is seen in virtually all the signals in the PMMA with the carbonyl being slightly more affected as discussed previously. Similar results are seen with PHEMA. Although the hydroxylated side chain in PHEMA might serve as a weak hydrogen-bond donor, neither

TABLE VIII

Effect of the relaxation agent on chemical shift of PMMA.

Assign.	Tacticity	no relax. agent *ppm*	0.025 M $Cr(acac)_3$ *ppm*	0.050 M Cr(acac) *ppm*	0.025 M $Fe(acac)_3$ *ppm*	0.050 M $Fe(acac)_3$ *ppm*
C = O	rr	177.89	177.65	177.46	177.60	177.51
	rr	177.60	177.37	177.17	177.32	177.22
	mr	176.89	176.68	176.48	176.63	176.53
	mr	176.73	176.51	176.31	176.45	176.36
	mm	175.94	175.74	175.55	175.68	175.59
CH_2		54.24	54.12	53.92	54.06	53.98
OCH_3		51.61	51.40	51.24	51.37	51.33
C quat.	mm	45.33	45.20	45.00	45.14	45.06
	mr	44.68	44.58	44.58	44.51	44.43
	rr	44.34	44.23	44.23	44.17	44.09
CH_3	end	29.40	29.21	29.21	29.17	29.10
CH_3	mm	20.86	20.77	20.77	20.72	20.64
	mr	18.54	18.43	18.43	18.39	18.31
	rr	16.25	16.21	16.21	16.17	16.10

TABLE IX

Effect of the relaxation agent on ^{13}C-chemical shifts of PHEMA.

Assign.	Tacticity	no relax. agent	0.025 M $Cr(acac)_3$	0.050 M Cr(acac)	0.025 M $Fe(acac)_3$	0.050 M $Fe(acac)_3$
C = O	rr	176.75	176.67	176.60	176.60	176.48
	rr	176.50	176.42	176.36	176.35	176.28
	mr	176.06	175.98	175.91	175.92	–
	mr	165.88	175.80	175.74	175.74	175.67
	mm					
$-OCH_2-$		65.73	65.67	65.62	65.63	65.58
$-CH_2OH$	58.35	58.30	58.26	58.31	58.28	
CH_2	52.92	52.80	52.74	52.73	52.70	
C quat.	mm					
	mr	44.54	44.46	44.39	44.44	44.37
	rr	44.19	44.11	44.05	44.10	44.03
CH_3	mm					
	mr	18.14	18.07	18.01	18.06	17.99
	rr	16.46	16.38	16.33	16.40	16.33

the T_l nor the change in chemical shift is affected more strongly than other resonances in the polymer. This indicates that there is no selective interaction occurring between the hydroxylated side chain and the relaxation agent. In the PHEMA/DMSO system, PHEMA probably cannot compete with DMSO for specific interactions with the relaxation agent.

Although Cr(III) is unusual in being relatively inert to substitution and oxidation or reduction reactions [5], complexes of acetonylacetone can undergo unwanted side reactions with acid (i. e., carboxylic) groups on the polymers. The polymer acid group can displace the acac group on the metal. This will cause the appearance of resonances due to acetonylacetone in the spectrum, and the loss of intensity in acid carbonyls in the polymer. The resonances of species directly bonded to the metal are sufficiently broadened that they are not observed in the ^{13}C-NMR spectrum. We have also observed the appearance of acetonylacetone resonances in the ^{13}C-NMR spectrum of anhydride containing polymers at 120°C as well as methacrylic acid copolymers. Presumably ring-opening of the anhydride occurs which allows reaction with the Cr(acac)$_3$. In some cases a precipitate may be formed upon interaction of an acid group in the polymer with the relaxation agent.

We generally recommend a temperature limit of 120°C when using Cr(acac)$_3$. Samples can be heated temporarily to higher temperatures (140–160°C) to aid in polymer dissolution. This heating appears to cause a temporary, reversible, color change in the Cr(acac)$_3$ solution from purple to brown or green. Solutions of Cr(acac)$_3$ should not be used if the color is not purple.

CONCLUSIONS

Several precautions should be observed when using Cr(acac)$_3$. The Cr(acac)$_3$ interacts fairly strongly with chlorinated and hydrogen-bonding solvents; changing to a solvent which interacts more strongly with the relaxation agent can increase the T_l^{obsvd} values of the polymer under study. An advantage to the use of such solvents is that they may prevent preferential interaction of the relaxation agent with, for example, certain tacticity sequences, end groups, etc. Cr(acac)$_3$ will also interact with hydrogen bonding or polar solutes, and the strength of this interaction can depend on the relative strength of the solvent interactions. Furthermore, Cr(acac)$_3$ will react irreversibly with polymer functional groups, such as acids, which can displace the (acac) group.

Given these precautions, relaxation agents can be extremely useful in obtaining quantitative ^{13}C-NMR data for polymeric systems. For acrylate polymers, 0.05 M Cr(acac)$_3$ will generally reduce all T_l values to less than 0.8 s. Thus a 5–8 *s* relaxation delay (with a 0.5 s acquisition time) is generally adequate with 0.05 M Cr(acac)$_3$. This is especially useful for studying mobile polymer sidechains, branches, and end groups. Cr(acac)$_3$ is preferred over Fe(acac)$_3$ for a variety of reasons, including greater chemical stability and the absence of line broadening effects. We also recommend that inverse-gated decoupling be used for all quantitative work.

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