# Analysis of the Phase Partitioning of Additives in Rubber-Modified Plastics

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**ABSTRACT:**   The phase partitioning of additives in polymer blends has a large impact on the performance of the blend. Therefore, it is necessary to be able to quantify the level of the additives in each phase. A $^1$H–NMR method is presented to determine the partitioning of additives between the rubber and rigid phases of a high-impact polystyrene (HIPS) material. In one case, a HIPS material was modified with 2,6-di-*tert*-butyl-4-methyl-phenol (Ionol, CAS# 128-37-OMF) as a stabilizer for both phases. HIPS materials with varying levels of Ionol were melt-blended by extrusion and the total level of additives was determined analytically for these standard materials. The $^1$H–NMR method was used to determine the level of Ionol in the poly(butadiene) rubber phase. The Ionol was found to preferentially partition into the rubber phase with a partition coefficient of about 2. A second example of the same concept, instead utilizing $^{13}$C–NMR, involved the analysis of the partition coefficient for both Tinuvin P and Tinuvin 770 (CAS# 2440-22-4 and 52829-07-9), partitioning between the rigid and rubber phases of an ethylene–propylene–diene-modified (EPDM) toughened styrene–*ran*–acrylonitrile (SAN) copolymer. The partition coefficient was determined to be 0.5 for Tinuvin P and 1.3 for Tinuvin 770. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1963–1970, 2001

**Key words:**   NMR; additives; phase partitioning; polymer blends

## INTRODUCTION

Low molecular weight additives are often added to polymers to serve such functions as plasticizers, flow aids, stabilizers, mold releases, and so forth.[1,2] In particular, additives may serve to stabilize the polymer against degradation in a number of hostile environments including high temperature, high shear processing, UV-radiation, and other weathering conditions. For multicomponent polymer systems such as blends, it is important to be aware of the partitioning of the additive between the various phases of the blend such that all the phases have adequate concentrations of the stabilizer. However, quantification of the partitioning of the additive between the phases of a blend is a daunting task.

Analysis of the partition coefficient of an additive between phases of a blend is difficult because the domain size of the blend is normally submicron in size. Therefore, physical separation of the phases of the blend is not an option and solvent separation will alter the partitioning of the additives. Because partition coefficients are difficult to determine analytically, they are often modeled using a Flory–Rehner type model.[3,4] The depression of glass-transition temperature ($T_g$) using torsion braid analysis,[5] the direct measurement of additive concentration between phases using

scanning electron microscopy with X-ray energy dispersive spectroscopy,[6–8] and other microscopy techniques[9] have been utilized to study phase partitioning of additives in a blend. Although these techniques are effective in certain circumstances, they either are experimentally complex or have other limitations that hinder their broad application.

An NMR technique is presented here for the determination of the phase partitioning of additives between the rubber and rigid phases of a rubber-modified polymer blend. In one case, the partitioning of 2,6-di-*tert*-butyl-4-methyl-phenol (Ionol[10]) between the rigid and rubber phases of a polystyrene (PS) rigid phase modified with a polybutadiene (PBD) rubber, Firestone DIENE 55 PBD,[11] was determined. In a second application, the partitioning of both Tinuvin P[12] and Tinuvin 770[12] between a SAN rigid phase and an EPDM rubber phase was determined.

Phases with different motional characteristics can be differentiated using solid-state NMR by the proper choice of experimental conditions. Rigid solids tend to have long spin lattice relaxation times and very broad lines, as large as 40 kHz.[13] They also cross-polarize very effectively because of the static dipolar interactions. Rubbery solids, on the other hand, possess much shorter spin lattice relaxation times, narrower lines, and do not cross-polarize well.[14,15] Therefore, rubbery solids can be detected quantitatively using single-pulse experiments. Magic-angle spinning or elevated temperatures can be used to further narrow the lines.

## EXPERIMENTAL

### NMR

Magic-angle spinning (MAS) $^1$H–NMR analysis was performed at 200 MHz using a Bruker MSL-200 NMR spectrometer (Bruker Instruments, Billerica, MA). Spectra were acquired at ambient temperature ($\sim$ 23°C) with exponential apodisation, 2 Hz broadening. Spinning rates ranged from 2.5 to 4 kHz. A one-pulse experiment was used to obtain the spectra with a 3-$\mu$s pulse (90° = 5 $\mu$s). A 5-s repetition rate was used, with a 10-kHz sweep width and 8K points. The sample, as a powder, was loaded into the 4-mm rotor for the analysis. The spin lattice relaxation times of the $^1$H resonances of the rubber and the Ionol were all determined to be under 0.5 s using the inversion recovery method.

The $^{13}$C–NMR analysis was performed at 75.7 MHz using a Nicolet NT-300 high-resolution NMR spectrometer (Nicolet Instruments, Madison, WI), under the following conditions: pulse width, 90°; delay time, 5 s; data acquisition size, 8K; accumulation time, 0.205 s; sweep width, 20 kHz; apodisation, 10 Hz; complete decoupling; and temperature, 110°C. The spin lattice relaxation times of all the carbons used for quantification were less than 1.2 s at this temperature for the Tinuvin–SAN–EPDM blends.

### Materials

The EPDM-modified SAN (SAN–EPDM) copolymers contained 23 wt % EPDM. The additives were blended into the polymer by melt-blending at 200°C. Concentrates of 4.6, 7.6, and 9.2 wt % for Tinuvin P and 6.1, 8.3, and 10.8 wt % for the Tinuvin 770 in SAN–EPDM were prepared. The total level of these additives was determined by liquid chromatography (LC).

The high-impact polystyrene (HIPS) material contained 9 wt % PBD, as well as Irganox 1076[12] and zinc stearate. The Ionol was added to the HIPS and the mixture was dry blended and then extruded. The following blends were made: 1.97, 3.85, 5.67, and 7.42 wt % Ionol.

Standard rubber–Ionol blends were also made to calibrate the NMR method. These were made by dissolving Ionol and the rubber in methylene chloride and stripping off the solvent. The level of Ionol in all the samples was determined by LC.
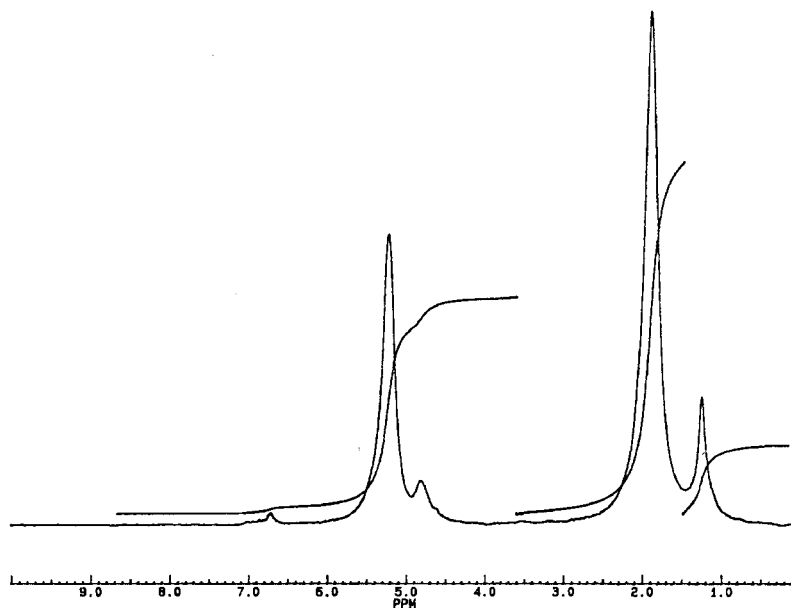
### Extrusion

The standards were produced using a $\frac{3}{4}$-in. Killion single-screw extruder equipped with three heating zones (375, 400, and 415°F) and a $\frac{1}{8}$-in. strand die (425°F). The extruded polymer strand was cooled by passing over an 8-in. chilled casting roll unit. A pelletizer was used to provide pellets for multiple passes of the polymer through the extruder. Three passes were performed on each standard.

### Analysis of Ionol

Approximately 1 g of each sample was dissolved with 5 mL chloroform. The bulk polymer was precipitated with 10 mL methanol. The extracts were diluted 1 : 10 with acetonitrile and analyzed by reverse-phase liquid chromatography (RPLC)

## Table I   Structures of the Additives

**Ionol**

**Tinuvin 770**

**Tinuvin P**

using a Hewlett–Packard 1090 liquid chromatograph (Hewlett–Packard, Palo Alto, CA) with diode array detector (DAD), equipped with a Zorbax C18 $4.0 \times 80$ mm column, $5\text{-}\mu$ packing.

## RESULTS AND DISCUSSION

### Ionol/HIPS

The structure of Ionol is given in Table I. The high-resolution ^{1}H–NMR spectrum of Ionol has resonances at 1.40 ppm (*t*-butyl methyl), 2.21 (methyl), 4.78 (aromatic protons), and 6.81 (phenolic proton).[16] The solid-state MAS ^{1}H–NMR spectrum of the HIPS material with no Ionol is given in Figure 1. The olefinic protons are observed between 4.5 and 5.5 ppm (*cis, trans,* and vinyl isomers) and the aliphatic protons at 1.7 to 3 ppm. A small shoulder at 1.4 ppm is observed in this spectrum, even though no Ionol is present, attributed to the *t*-butyl protons of Irganox 1076, which is octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate. Its contribution must be subtracted from the area of the Ionol *t*-butyl resonance.

Figure 2 shows the solid-state MAS ^{1}H–NMR spectrum of a PBD standard with 7.3 wt % Ionol present, as determined by LC. The resonance at 1.4 ppm is much larger in this spectrum because of the presence of Ionol. The protons of the PBD



**Figure 1**   The solid-state ^{1}H–NMR spectrum of the HIPS sample with no Ionol added.

**Figure 2** The solid-state $^1$H–NMR spectrum of the PBD standard with 7.3 wt % Ionol added.

obscure the resonances of the other Ionol protons. The level of Ionol in the rubber phase was determined from the ratio of the *t*-butyl protons at 1.4, with the contribution from the *t*-butyl protons of Irganox 1076 subtracted, to the area of the methylene protons of the PBD corrected for the 4-methyl protons of Ionol. This technique gave a level of 7.9 wt % Ionol in the rubber, in close agreement with the LC analysis. A series of standards were prepared of Ionol in polybutadiene ranging from 0 to 7.3 wt %. Table II shows the actual levels found by NMR versus those determined by LC. The agreement is excellent, with a precision of about 0.5 wt % absolute. A plot of these results is given in Figure 3.

The solid-state $^1$H–NMR spectrum of the HIPS material with nominally 6 wt % Ionol is given in

Figure 4. The level of Ionol in the rubber phase was determined by NMR as described earlier. Table III and Figure 5 give the Ionol levels in the HIPS as determined by LC and the levels found in the rubber phase by NMR.

The partition coefficient is defined as the ratio of the concentration of the Ionol found in the rubber phase to that found in the rigid PS phase. Because the level of Ionol in the rubber phase can be determined from $^1$H–NMR and the total amount in the HIPS is also known (determined by

**Table II  Weight Percentage Ionol in Polybutadiene Standards**

| Weight Percentage Ionol by LC | Weight Percentage Ionol by NMR |
|---|---|
| 0.0000 | 0.0000 |
| 0.12000 | 0.20000 |
| 0.65000 | 1.0000 |
| 0.70000 | 1.3000 |
| 6.4000 | 6.1000 |
| 7.3000 | 7.9000 |
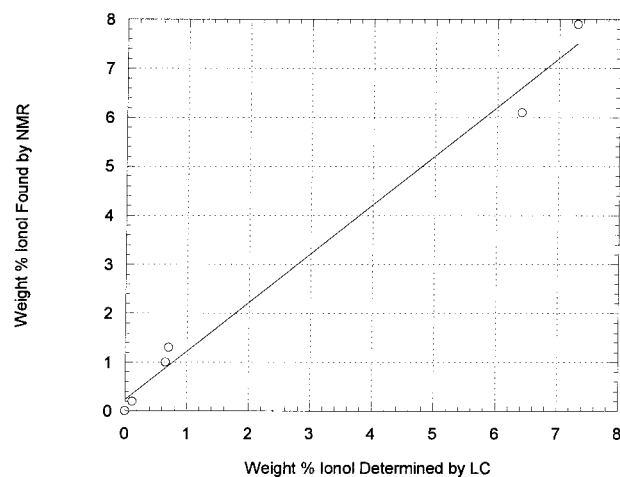


**Figure 3** Weight percentage of Ionol in polybutadiene standards as determined by LC and $^1$H–NMR.
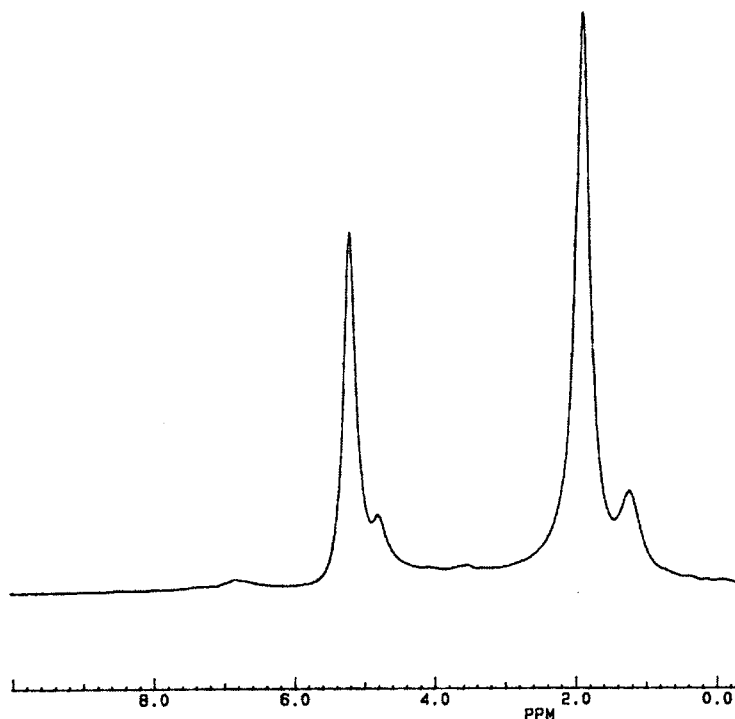
**Figure 4**   The solid-state $^1$H–NMR spectrum of the nominally 5.67 wt % Ionol in the HIPS sample.

LC), as is the level of rubber in the HIPS (9 wt %), the concentration of Ionol in the PS phase can be calculated by the difference. The ratio of these concentrations is the partition coefficient. Table III also lists the concentration of Ionol in the PS phase, calculated by subtracting the level in the PBD from the total concentration in the HIPS, and the calculated partition coefficient for each sample. The average of these values is 2.0 and the estimated precision of these values is ±0.4. The value of 2.9 determined at low loadings of Ionol is

probably attributable to the precision of determining Ionol by $^1$H–NMR at that low loading. The partition coefficient is fairly constant at 1.6 to 1.9 for the samples from 3.5 to 7.3 wt % Ionol, indicating the rubber phase is not being saturated.

**Tinuvin/SAN–EPDM**

Figure 6 shows the $^{13}$C–NMR spectrum of a SAN–EPDM system without any additives, heated to 110°C. Only the EPDM rubber is observed: the

**Table III   Weight Percentage Ionol in HIPS Standards**

| Nominal Ionol in the HIPS (wt %) | Ionol Found in the HIPS by LC (wt %) | Ionol Found in the Rubber Phase of the HIPS by NMR (wt %) | Ionol in the Poly(styrene) Phase by Difference (wt %) | Partition Coefficient[a] |
|---|---|---|---|---|
| 0.0 | 0.0 | 0.0 | NA | NA |
| 1.97 | 1.6 | 4.0 | 1.4 | 2.9 |
| 3.85 | 3.5 | 5.3 | 3.3 | 1.6 |
| 5.67 | 5.3 | 9.4 | 4.9 | 1.9 |
| 7.42 | 7.3 | 11.0 | 6.9 | 1.6 |
| | | | | 2.0 ± 0.4 |

[a] Determined by (ionol concentration in PBD) ÷ (ionol concentration in PS).
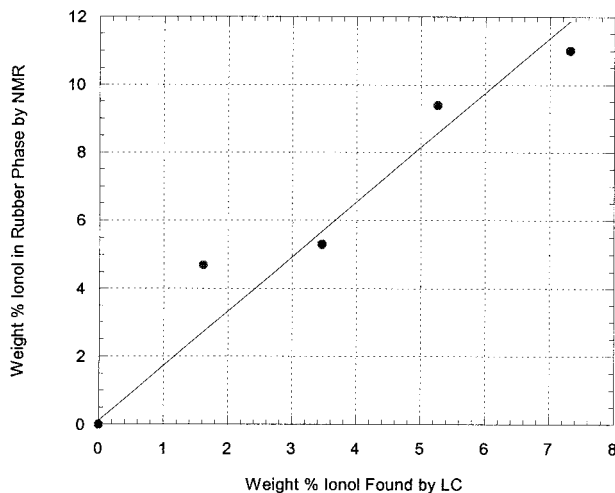
**Figure 5** The level of Ionol determined in the HIPS by LC and in the rubber phase of the HIPS by NMR.

olefinic carbons of the ethylidene norbornene at 110.5 and 146.9 ppm and the aliphatic carbons of the EPDM copolymer between 10 and 50 ppm. The $^{13}$C–NMR spectrum of a SAN copolymer with 10 wt % Tinuvin P under the same experimental conditions was also performed. This spectrum showed resonances from a long-chain aliphatic component and OCH$_2$ functionality only. Broad aromatic resonances were also observed that possibly resulted from oligomers. However, there was no indication of Tinuvin P in this spectrum, as expected, because there is not enough molecular motion in this glassy phase at 110°C to give narrow NMR lines. Thus the spectra of the blanks confirm that there are no interferences to the analysis of Tinuvin P in either the rubber phase or the SAN phase.
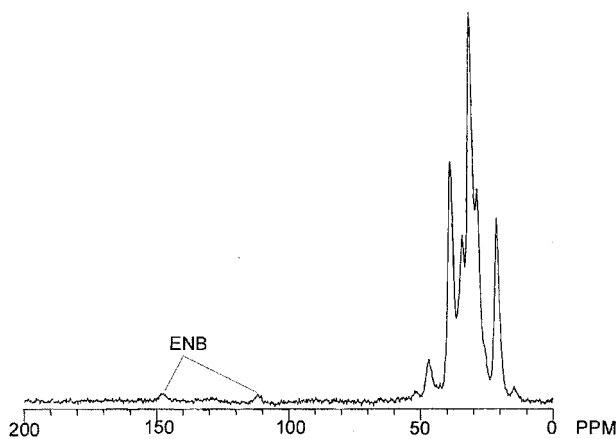


**Figure 6** The $^{13}$C–NMR spectrum of SAN–EPDM rubber with no additives at 110°C.
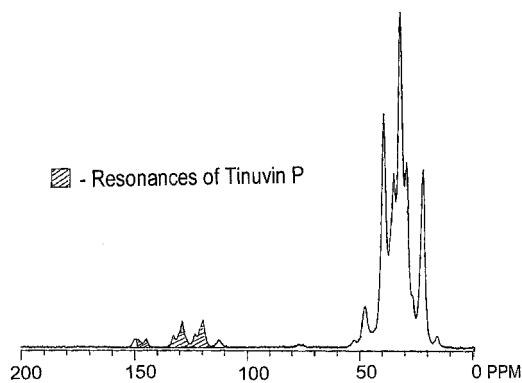


**Figure 7** The $^{13}$C–NMR spectrum of EPDM rubber with nominally 10 wt % Tinuvin P, 100°C.

The $^{13}$C–NMR spectrum of EPDM rubber with 10 wt % Tinuvin P added by solution blending is given in Figure 7. The aromatic resonances of Tinuvin P are clearly observable in this spectrum. The ratio of the areas of these aromatic carbons (with the contribution of the olefinic carbons of EPDM subtracted) to the area of the EPDM aliphatic carbons was utilized to calculate the level of Tinuvin P in the rubber. The level was determine to be 8.6 wt % by this method (see Table IV).

Figure 8 shows the temperature dependence of the $^{13}$C–NMR spectrum of a SAN–EPDM concentrate with roughly 5 wt % Tinuvin P added. As the temperature is increased above room temperature, the resonances narrow until about 110°C, above which the lines do not narrow significantly. At 150°C, contributions from the aromatic carbons of the rigid phase become apparent as a broad hump on the baseline. Therefore, the analysis temperature was chosen as 110°C, given that the resonances of the rubber phase were sufficiently narrow and the contribution from the rigid phase was minimum. Phasing errors and broad humps such as that in the 150°C spectrum were eliminated by baseline correction methods.

Several SAN–EPDM polymer–Tinuvin P concentrate samples were blended as standards for the analysis. The concentration of Tinuvin P in these standards was analyzed by LC. They were then analyzed by the NMR method for the level of the additive in the rubber phase (see Table IV). A plot of the level of Tinuvin P found in the rubber phase by NMR versus the total level added to the SAN–EPDM blend is given in Figure 9. This plot indicates that the Tinuvin P preferentially partitioned into the rigid phase.

The analysis was also performed with Tinuvin 770 concentrates. The OCH$_2$ and carbonyl reso-

**Table IV   Level of Additive Determined in the Rubber Phase of SAN–EPDM Concentrates as a Function of Total Additive Level**

| Sample | Total Weight Percentage (LC) | Weight Percentage in Rubber (NMR) | Weight Percentage in SAN (by Difference) | Partition Coefficient[a] |
|---|---|---|---|---|
| EPDM concentrate | 10 | 8.6 | — | |
| SAN blank | 0 | ND[b] | 0 | |
| SAN–EPDM blank | 0 | ND[b] | 0 | |
| Tinuvin P concentrates | 4.6 | 2.3 | 5.21 | 0.4 |
| | 7.6 | 3.5 | 8.69 | 0.4 |
| | 9.2 | 5.9 | 10.08 | 0.6 |
| Tinuvin 770 concentrates | 6.1 | 7.6 | 5.70 | 1.3 |
| | 8.3 | 9.4 | 8.01 | 1.2 |
| | 10.8 | 13.5 | 10.08 | 1.4 |

[a] Determined by (additive concentration in EPDM) ÷ (additive concentration in SAN).
[b] ND, not detected at about 0.5 mol %.

nances of Tinuvin 770 were used for quantitation. The level of Tinuvin 770 added to the SAN–EPDM concentrates versus that found in the rubber phase is also given in Table IV and Figure 9. Tinuvin 770 preferentially partitioned into the rubber phase.

The analysis of Tinuvin P and Tinuvin 770 was also attempted using $^1$H–NMR spectroscopy be-

cause the inherent sensitivity of this method is much better than that of $^{13}$C–NMR spectroscopy. Unfortunately, the $^1$H–NMR resonances of the EPDM rubber did not narrow sufficiently with temperature to make the analysis possible. $^{13}$C–NMR spectroscopy, which has a 20-fold resolution advantage over that of $^1$H–NMR, made this analysis possible.
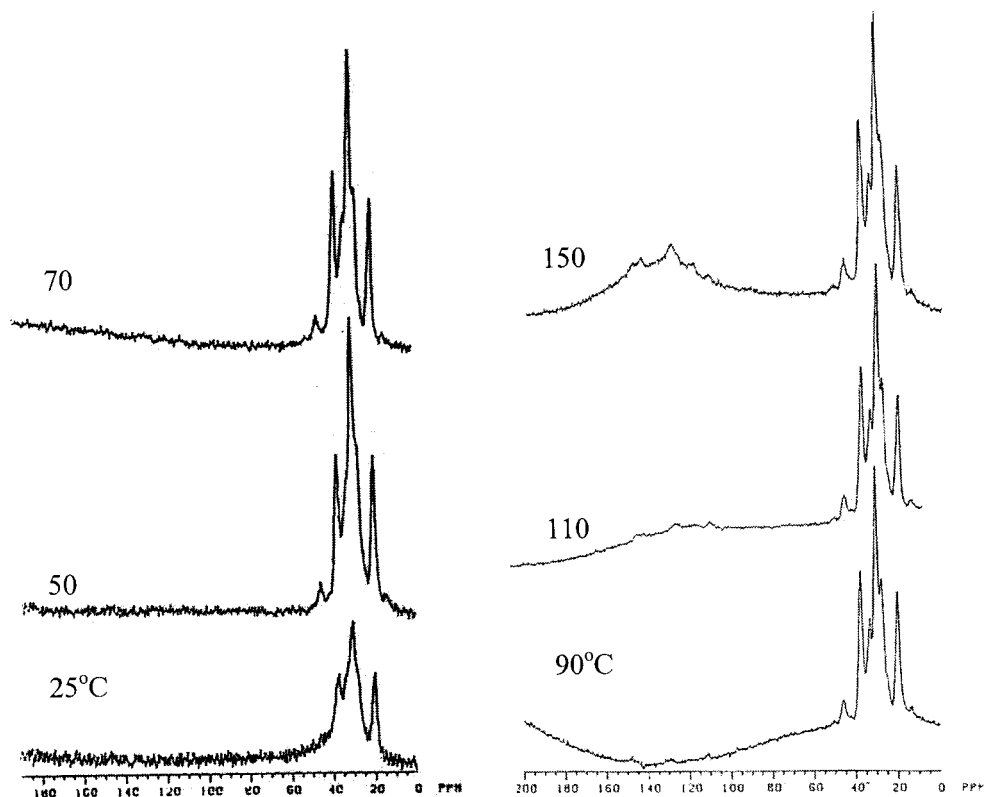


**Figure 8**   The $^{13}$C–NMR spectra of the SAN–EPDM as a function of temperature.
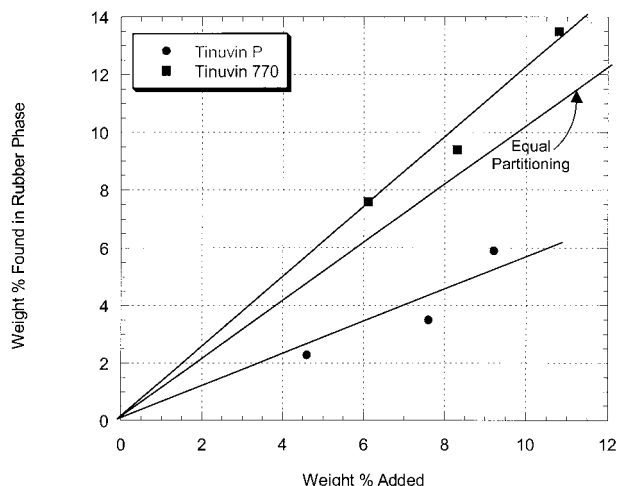
**Figure 9** The level of Tinuvin P and Tinuvin 770 determined in the SAN–EPDM by LC and in the rubber phase of the SAN–EPDM by NMR.

## CONCLUSIONS

The ability of NMR to differentiate phases based on molecular mobility was the basis for these methods. The rubbers, having higher mobility than that of the rigid matrix, gave narrow, almost high-resolution, NMR lines under solid-state NMR conditions. The components dissolved in the rubber phase shared the motional characteristics of the rubber and also could be quantified. This study demonstrated that the NMR approach was not only successful in observing the additives but could also be used as an absolute method for their quantitation.

Two examples of this method were presented. In one case, the partition coefficient for Ionol between the rigid and rubber phases of a HIPS material was determined by $^1$H–NMR spectroscopy. Ionol was found to preferentially partition into the rubber phase with a partition coefficient of about 2. This has obvious, but nonetheless, serious ramifications concerning the stabilization of the PS phase.

$^{13}$C–NMR spectroscopy was used in a second case to determine the partitioning of Tinuvin P and Tinuvin 770 between the rigid and rubber phases of SAN–EPDM. The partition coefficients determined from NMR were 0.5 ± 0.1 (preferentially partitions into the rigid phase) and 1.3 ± 0.1 (preferentially partitions into the rubber phase) for Tinuvin P and Tinuvin 770, respectively. This analysis was performed on samples with unrealistically high levels of additives. However, the plots of the level of additive found in the rubber phase versus the total amount added to the blend system indicated that, even at these high levels, the phases were not being saturated. Saturation would have been indicated by a nonlinearity in the plot of Figure 9 at high additive concentrations. Therefore, the partition coefficients calculated from these data appear to be valid at low additive concentrations because the partitioning is governed by equilibrium thermodynamic considerations.

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