Thermal Decomposition of Polyisoprene, Poly(p-isopropyl α-Methylstyrene), and Poly(isoprene/p-isopropyl α-Methylstyrene)

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ABSTRACT

Thermal decompositions of polyisoprene, poly(p-isopropyl α-methylstyrene) (PPIPαMS), and poly(isoprene/p-isopropyl α-methylstyrene) (sample M-32) were carried out at various temperatures in the range 200-340°C in a differential thermo-gravimetric apparatus. The undecomposed polymers as well as their decomposed residues were analyzed by gel-permeation chromatography (GPC), infrared spectroscopy (IR), and nuclear magnetic resonance (NMR). Based on the changes observed in the distribution of molecular weights, depolymerization is the predominant step in the decomposition of PPIPαMS and polymer M-32, whereas random scissions predominate in the case of polyisoprene. The combined data of GPC, IR, and NMR indicate that only interchain reactions leading to the formation of cyclized products are present in the decomposition

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of polyisoprene while interchain as well as intrachain reactions
are operative in the case of polymer M-32.

INTRODUCTION

Studies on the thermal degradation of natural rubber (cis-polyiso-
prene) [1-6] revealed that in the temperature range 200-300°C low
molecular weight materials were formed and that the residual rubber
became progressively insoluble and intractable. Above 300°C degra-
dation was rapid, leading, in the vicinity of 400°C, to complete
volatilization of the sample in a period of approximately 30 min. It
was postulated that the degradation process involves random scissions
and intermolecular transfer reactions which eventually yield poly-
cyclic structures.

The thermal decomposition of branched poly(p-isopropyl α-
methylstyrene) (PPIPαMS) in the range 150-400°C was reported
earlier from this laboratory [7]. At temperatures below 200°C,
weight losses on the sample were not significant; however, the $\bar{M}_w$

values were found to increase, indicating the possibility of cross-
linking. Between 200 and 400°C, weight losses on decomposition be-
came more and more important leading, as in the degradation of
rubber, to complete volatilization of the sample in less than 50 min
at 400°C. The process responsible for these decompositions, as
established by GPC molecular weight distributions, was that of
depolymerization.

One notes that these two homopolymers decompose via different
routes but have the same tendency to form crosslinked structures.
Thus, it was thought of interest to explore the decomposition of the
products resulting from the simultaneous polymerization of isoprene
with p-isopropyl α-methylstyrene and compare their data with those
obtained on the decomposition of polyisoprene and PPIPαMS. The
principal results of these studies are outlined in the following
sections.

EXPERIMENTAL

Materials

p-Isopropyl α-methylstyrene (PIPαMS) (Aldrich Chemical Co.) was
kept over calcium hydride and degassed on a vacuum line for two weeks.
It was distilled under vacuum, but the head and tail fractions were

discarded. Vapor-phase chromatography of the middle fraction
showed that there were no impurities present. Before use, the mono-
mer was further purified by distilling it on to a mirror of sodium.
Isoprene (Aldrich Chemical Co.) was purified in the same manner.

n-Butyllithium (BuLi) (Foote Mineral Co.), received as a 15%
solution in cyclohexane, was used as such without further purification.
N,N,N',N'-Tetramethyl-1,2-ethylenediamine (TMEDA) (Aldrich Chemi-
cal Co.) was dried over Molecular Sieves and distilled as required on
a vacuum line prior to use.

The cis- and trans-polyisoprene samples were provided by Aldrich
Chemical Company and were used as received.

Polymerization Procedure

Bulk anionic polymerization of a mixture of the PIPαMS and isoprene
monomers with BuLi-TMEDA complex as initiator was carried out in
a screw-capped reactor placed inside a dry box. The reactor was
washed with a sodium dichromate-sulfuric acid solution, rinsed with
distilled water, then methanol, and finally dried in an oven prior
to storing in an atmosphere of nitrogen. Isoprene, PIPαMS, TMEDA,
and BuLi were injected into the reactor in that order until the red
color persisted. The reactor was rapidly closed and immersed in a
bath set at -25°C for 24 hr. After the reaction was over, the polymer
was precipitated out of the solution with methanol: it was filtered off
then dried in a vacuum oven at 60°C.

Analysis of the Polymers

Thermogravimetry (TGS).   A Perkin-Elmer TGS-1
thermogravimetric scanning balance, operating in a pure dry nitrogen
atmosphere at a heating rate of 20°C/min, was used to follow the de-
composition of 2 mg samples of the polymer [7]. Nitrogen was made
to flow continuously through the apparatus to flush out the volatile
degradation products.

Differential Scanning Calorimetry (DSC).   A Perkin-
Elmer Model DSC-2 differential scanning calorimeter was also used
to decompose polymer samples (10 mg) at the same heating rate
(20°C/min) [7] but under a pure dry helium atmosphere.

Gel-Permeation Chromatography (GPC).   Molecular
weight distribution analyses of the polymer samples both before and
after decomposition were carried out with a Waters Associates model
200 GPC operated in a constant temperature room (25 ± 0.5°C). The
separating system consisted of five 8 × 1200 mm columns connected
in series, each packed with crosslinked polystyrene gel having (by

the Waters method) pore sizes of 1×10^6, 1.5×10^5, 3×10^3, 250, and 60 Å, respectively. The flow of solvent, tetrahydrofuran degassed with nitrogen, was maintained at 1 ml/min while the concentration of the polymer in the samples was limited to 1/4 of 1 wt % in order to render negligible "concentration effects" on the peak position in the chromatograms. Calibration of the instrument was performed with low polydispersity PPIPαMS samples whose $\overline{M}_w$ and $\overline{M}_n$ values were calculated from light scattering and membrane osmometry data, respectively [8], and with polyisoprene samples (Aldrich Chemical Company) whose $\overline{M}_w$ and $\overline{M}_n$ values were determined by viscometry [9, 10] and osmometry, respectively. Molecular weights were then computed by the summation method [11]. The calibration curve used for the calculation of $\overline{M}_w$ and $\overline{M}_n$ values for the undecomposed and de-composed samples of polymer M-32 were established from those of polyisoprene and PPIPαMS. For example, at the elution count of 30, $\overline{M}_w$ of polyisoprene is 1.9×10^5 ($\overline{DP}$ = 2800), $\overline{M}_w$ of PPIPαMS 1.2×10^4 ($\overline{DP}$ = 75), and that of M-32 (3 units of isoprene + 2 units of PIPαMS), 1.2×10^5 ($\overline{DP}$ = 1130). Values of the average degree of polymerization $\overline{DP}$ for polymer M-32 were reached by assigning an average value of 105 [$(3 \times 68 + 2 \times 160)/5$] to a single monomer unit.

Viscosity

Viscosity-average molecular weights of cis-polyisoprene and trans-polyisoprene were computed from their respective limiting viscosity number [η] measured at 30°C in toluene [9] and 32°C in benzene [10] by using an Ubbelohde viscometer.

Infrared Spectroscopy

IR spectra of the polymers on KBr pellets and in the form of thin films (cast from benzene solutions) were recorded with a Beckman-12 infrared spectrophotometer and analyzed by using the characteristic wavenumbers of linear and cyclized polyisoprenes [12-20] and PPIPαMS [21].

Nuclear Magnetic Resonance Spectroscopy

NMR spectra of the polymer solutions (15% w/v in o-dichloro-benzene) at 100°C and (in carbon tetrachloride) at 75°C were recorded

TABLE 1. Thermogravimetric and GPC data on Undecomposed and Decomposed Samples of Polyisoprene and PPIPαMS [7]

Sample	Decomposition temperature (°C)	Weight loss (%)	$\overline{M}_w \times 10^{-3}$ (GPC)	$\overline{M}_n \times 10^{-3}$ (GPC)	$\overline{P}_d$ [a]
CIS-1	Undecomposed	0	1150	672	1.7
CIS-2	300	6	221	123	1.8
CIS-3	320	20	137	50	2.7
CIS-4	330	40	57	21	2.7
CIS-5 .	340	60	-	-	-
TRANS-6	Undecomposed	0	526	304	1.7
TRANS-7	300	10	148	60	2.5
TRANS-8	320	22	94	33	2.8
TRANS-9	330	42	-	-	-
TRANS-10	338	55	59	20	3.0
S-10-0	Undecomposed	0	12	10.4	1.15
S-10-3	200	1	13	9.3	1.4
S-10-4	225	3	13	9.3	1.4
S-10-5	250	6	14	10.0	1.4
S-10-6	275	11	14	9.3	1.5
S-10-7	290	22	13	8.1	1.6
S-10-8	300	36	13	8.1	1.6

[a]$\overline{P}_d$ is defined as $\overline{M}_w$(GPC)/$\overline{M}_n$(GPC).

with a Varian Associates 220 MHz spectrometer, tetramethylsilane being used as the internal standard. Analysis of the spectra was made with the help of proton assignments for polyisoprene [19, 20, 22-24] and PPIPαMS [25].

RESULTS AND DISCUSSION

Decomposition of Polyisoprene

In Table 1 are summarized for the case of cis-polyisoprene (CIS-1) (structure I) and trans-polyisoprene (TRANS-6) (structure II) values
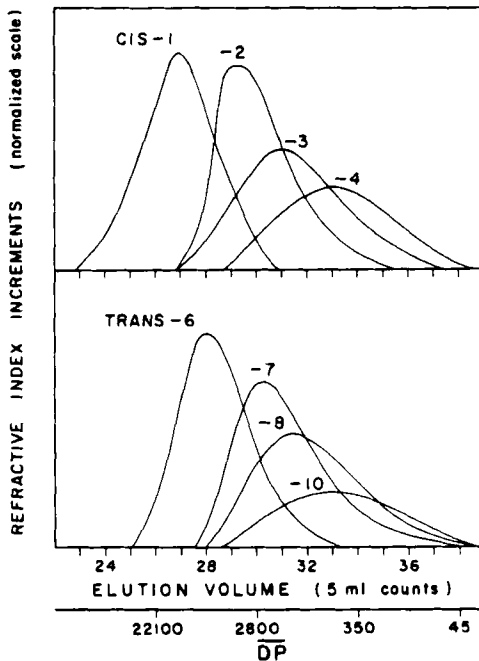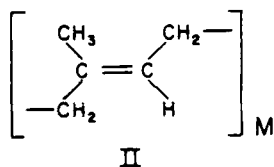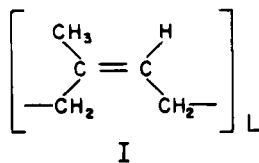
FIG. 1. GPC molecular weight distributions of cis-1,4-polyisoprene (CIS-1) and trans-1,4-polyisoprene (TRANS-6) samples subjected to isothermal treatments for 50 min at different temperatures. (See Table 1 for other data.)

of the percent weight loss (α), the GPC molecular weights ($\overline{M}_w$ and $\overline{M}_n$) and the polydispersity ($\overline{P}_d$)—calculated from the curves shown in Fig. 1—obtained both before and after samples of the polymers were subjected to 50 min isothermal decomposition. In both cases, the values of $\overline{M}_w$ and $\overline{M}_n$ decrease and those of $\overline{P}_d$ increase with increasing values of α.

In the case of sample CIS-1 ($\overline{M}_w = 11.5 \times 10^5$ and $\overline{M}_n = 6.72 \times 10^5$), heating at 300°C for a period of 50 min resulted in a weight loss of only 6% but the decomposed product CIS-2 showed a fivefold decrease in molecular weights, ($\overline{M}_w = 2.21 \times 10^5$, $\overline{M}_n = 1.23 \times 10^5$). The value of $\overline{P}_d$, however, did not vary by much. Isothermal treatments at 320 (CIS-3) and 330°C (CIS-4) yielded α values of 20 and 40% and the

$$\left[\begin{array}{c} \underset{-CH_2}{\overset{CH_3}{C}} = \underset{CH_2-}{\overset{H}{C}} \end{array} \right]_L$$

I

$$\left[\begin{array}{c} \underset{-CH_2}{\overset{CH_3}{C}} = \underset{H}{\overset{CH_2-}{C}} \end{array} \right]_M$$

II

decomposed products had respective $\overline{M}_w$ of 1.37×10^5 and 5.7×10^4 and $\overline{M}_n$ of 5.0×10^4 and 2.1×10^4. The $\overline{P}_d$ values increased from 1.7 in CIS-1 to 2.7 in CIS-3 and CIS-4.

In the case of sample TRANS-6 ($\overline{M}_w = 5.26 \times 10^5$ and $\overline{M}_n = 3.04 \times 10^5$) heating at 300°C for a period of 50 min resulted in a slightly larger 10% weight loss, but as in the case of the CIS-1 sample, the decomposed product (TRANS-7) had nearly a fivefold decrease in molecular weights and showed values of $\overline{M}_w = 1.48 \times 10^5$, $\overline{M}_n = 6.0 \times 10^4$, and $\overline{P}_d = 2.5$. Isothermal treatments at 320 (TRANS-8) and 338°C (TRANS-10) yielded α values of 22 and 55%, and the decomposed products had respective $\overline{M}_w$ of 9.4×10^4 and 5.9×10^4 and $\overline{M}_n$ of 3.3×10^4 and 2.0×10^4. The $\overline{P}_d$ increased from 1.7 in TRANS-6 to 2.8 in TRANS-8 to 3.0 in TRANS-10.

The normalized GPC molecular weight distributions of undecomposed and decomposed samples of cis- and trans-polyisoprene shown in Fig. 1 resemble those obtained in the case of polystyrene decomposition [26], where the process involved was established to be that of random scissions for $\alpha < 10\%$ and random scissions plus depolymerizations for $\alpha > 10\%$. In the case of the decomposition of polyisoprene where for $\alpha < 10\%$ there was a fivefold decrease in the molecular weights, the most likely process involved is that of random scissions. The process whereby the decomposition of a high molecular weight polymer with a $\overline{P}_d$ of 2.0 or less leads to products of lower molecular weight with a most probable distribution, has been attributed to random scissions by Berlin and Yenikolopyan [27]. The high $\overline{P}_d$ values in some of the decomposed products of cis- and trans-polyisoprene may arise out of intrachain or interchain crosslinking
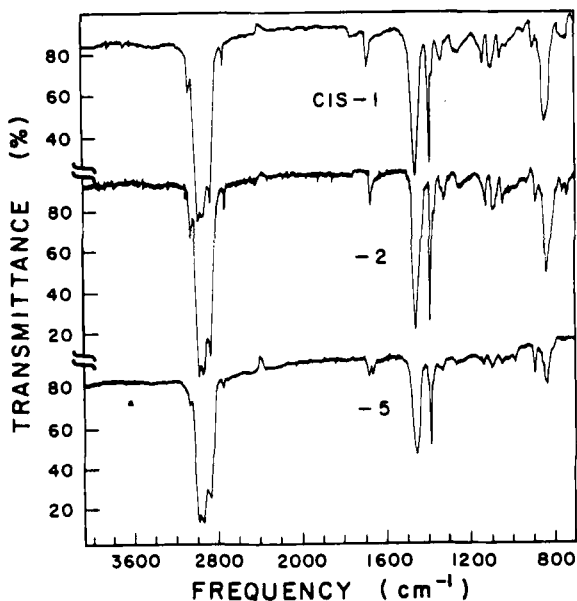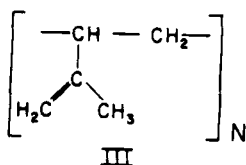
FIG. 2. IR spectra of undecomposed and decomposed samples of cis-1,4-polyisoprene. (See Table 1 for other data.)

reactions which result in an increase in the $\overline{M}_w$ values and consequently an increase in $\overline{P}_d$. The presence of such reactions has been suggested by the data obtained with NMR spectroscopy in the present study.

In Fig. 2 are presented the IR spectra of undecomposed (CIS-1) and decomposed (CIS-2, CIS-5) samples of cis-polyisoprene. The spectrum of CIS-1 shows important peaks at the following wave numbers (cm^{-1}): 2960 (ν_{as} CH$_3$), 2925 (ν_{as} CH$_2$), 2850 (ν_s CH$_2$), 1660 ($\nu_{C=C}$), 1460 (δ_{as} CH$_3$ and δ_s CH$_2$), 1380 (δ_s CH$_3$), 1315 [=CH− vibration of cis- C(CH$_3$)=CH−], 1130 [C−CH$_3$ vibration of cis-C(CH$_3$)=CH group] [13-17], 1250, 1090, 1040 (cyclized products [16, 17]), 890 [δ_{CH_2} of CH$_2$=C(CH$_3$)] [12-20], and 840 [δ_{CH} out-of-plane of cis −C(CH$_3$)=CH−] [12-20]. The IR spectra of decomposed polymers were frequently recorded from thin films cast out of benzene solutions. The choice of benzene as solvent was made primarily because o-dichlorobenzene was used for the NMR spectra obtained with

the same decomposed products. Thus any peaks appearing at wave-numbers of 1620, 1500, 1480, 740, and 720 cm^{-1} are due to the solvent and must be discarded.

A comparison of the IR spectrum of the CIS-1 with those of the CIS-2 and CIS-5 samples revealed the following. (a) The ratio of peak intensities at wavenumbers (cm^{-1}) 2960/(2925 and 2850) correspond-ing to total stretching vibrations of $-CH_3$ and $-CH_2-$ groups, respec-tively, remains constant at 0.54 even after decomposition at 340°C (CIS-5). (b) The ratio of peak intensities at wavenumbers (cm^{-1}) 1660/(2925 and 2850) and 1660/2960 for CIS-1, CIS-2, and CIS-5 samples, were 0.104, 0.094, 0.055 and 0.19, 0.18, 0.10, respectively. In the CIS-5 sample, however, there was doubling of the $C=C$ absorbance band with the appearance of a new peak at 1650 cm^{-1}: in this case 1650/(2925 and 2850) and 1650/2960 were 0.55 and 0.10, respectively. This would suggest that rearrangement of cis-1,4 polyisoprene to structures, carrying isopropenyl groups similar to those present in 3,4 polyisoprene (structure III) is occurring. (c) The ratio of peak intensities at wavenumbers (cm^{-1}) 1315/(2925 and 2850) and 1130/(2925 and 2850) in the CIS-1, CIS-2, CIS-5 samples were 0.091, 0.078, 0.044 and 0.10, 0.10, 0.044, respectively, indicating a decrease in the cis-1,4 structure of the polymers. (d) The intensity of the bands at wavenumbers (cm^{-1}) 1250, 1090, and 1040 attributed to cyclized structures [16-20] decreases on decomposition. This would suggest that certain cyclized products present in the original cis-1,4 polyisoprene decompose following thermal treatment. (e) The ratio of peak intensities at wavenumbers (cm^{-1}) 890/840 for CIS-1, CIS-2, CIS-5 were found to be 0.28, 0.30, and 0.68, respectively. This suggests that transformation of cis-1,4 polyisoprene into struc-tures resembling the 3,4-polyisoprene (structure III) [18-20] is taking place.

III

In Fig. 3 are presented the IR spectra of undecomposed (TRANS-6) and decomposed (TRANS-8 and TRANS-10) trans-1,4 polyisoprene samples. The highlights of the spectrum of TRANS-6 are similar to those of the CIS-1 except for the following: (1) the absence of peaks at wavenumbers (cm^{-1}) 1660, 1315, 1250, and 1130 and the presence of peaks at 1675 ($\nu_{C=C}$) and 1200, 1150, and 1100 (cyclized structures)
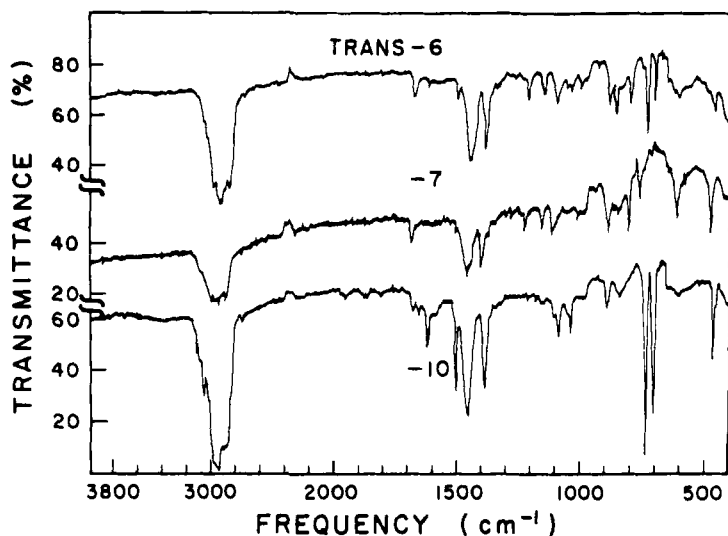
FIG. 3. IR spectra of undecomposed and decomposed samples of trans-1,4-polyisoprene. (See Table 1 for other data.)

and (2) the ratio of peak intensities at wavenumbers 890/840 which was 0.26 for CIS-1 is now 1.4 for TRANS-6.

A comparison of the spectrum of TRANS-6 with those of TRANS-8 and TRANS-10 revealed the following information. (a) The ratio of peak intensities at wavenumbers (cm^{-1}) 2960/(2925 and 2850) remains constant at 0.50. (b) The ratio of peak intensities at wavenumbers (cm^{-1}) 1675/(2925 and 2850) of 0.12 does not vary with decomposition although, as in the CIS-5 sample, in TRANS-10 doubling of the C=C absorbance band takes place, resulting in a new peak at 1650 cm^{-1}, suggesting structural transformations of the TRANS-6 sample to structures resembling 3,4-polyisoprene. (c) The intensity of the bands at wavenumbers (cm^{-1}) 1200, 1150, and 1100 decreases, whereas additional intense peaks at 1040 and 1090 appear in the TRANS-10 sample following decomposition at 340°C. This would suggest that certain cyclic products present in TRANS-6 decompose on thermal treatment while other cyclic arrangements are taking place. (d) The ratio of peak intensities at wavenumbers (cm^{-1}) 890/840 remains constant at 1.4 even after decomposition at 338°C.

These observations suggest that, on thermal treatment of trans-polyisoprene, structural rearrangements take place which may or may not be similar in nature to those observed during the decomposition of cis-polyisoprene.

Cyclization of cis- and trans-1,4 polyisoprene with H_2SO_4 [17], with $TiCl_4$[18], and radiation [20] are known. It has been postulated that in such cyclization reactions, protonation of the double bond in the chain takes place. The adjoining double bond in the chain is then polarized and a new bond closing the ring is formed. The positive charge then transfers to the carbon atom of the next double bond [17-19]. This is followed by a proton abstraction and formation of a new double bond. The presence of these cyclic products in the polymer can be confirmed from their characteristic bands in the IR spectrum at wavenumbers (cm^{-1}), 1265, 1200, 1090, 1040, and 820. In the present study, the decomposed products CIS-2 and CIS-5 did not carry the characteristic bands mentioned above indicating that their structural transformations may be of a different nature than those reported in the literature [17, 18, 20]. In the case of decomposed trans-1,4-polyisoprene (TRANS-10) additional bands were noted at wavenumbers (cm^{-1}) 1040 and 1090; hence TRANS-10 may contain cyclic products similar to those found on the H_2SO_4 treatment of polyisoprene [17].

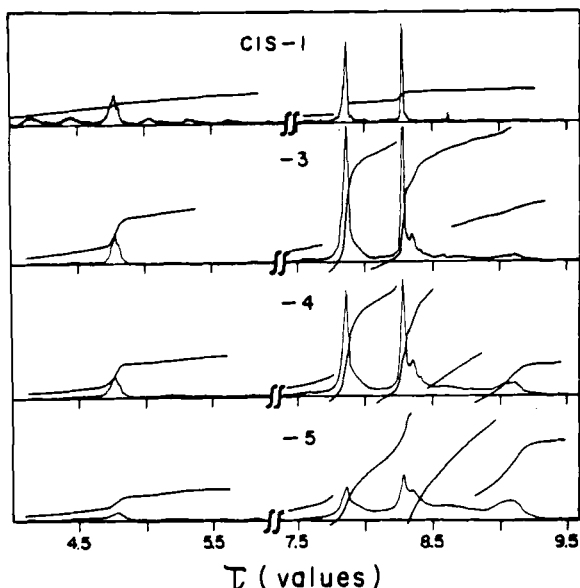In Fig. 4 are shown the NMR spectra of undecomposed (CIS-1) and

FIG. 4. NMR spectra of undecomposed and decomposed samples of cis-1,4-polyisoprene observed in o-dichlorobenzene at 100°C. (See Table 2 for other data.)

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TABLE 2. Apparent (A) and Normalized (N) Intensities of Methine ($=CH-$), Methylene ($-CH_2-$), and Methyl ($-CH_3$) Protons of Undecomposed and Decomposed Samples of Cis- and Trans-Polyisoprene

Sample	=CH-				-CH₂-						-CH₃			
	4.5-5.0 τ		5.0-5.5 τ		5.5-6.0 τ		7.5-8.1 τ		8.1-8.5 τ		8.5-8.9 τ		8.9-9.5 τ	
	A	N	A	N	A	N	A	N	A	N	A	N	A	N
CIS-1	1.0	1.0	-	-	-	-	4.0	4.0	3.0	3.0	-	-	-	-
CIS-2	1.0	0.9	-	-	-	-	4.0	3.8	3.0	2.8	-	-	-	-
CIS-3	0.8	0.6	-	-	0.2	0.2	3.1	2.5	2.9	2.3	0.5	0.4	0.4	0.3
CIS-4	0.7	0.4	-	-	0.1	0.1	2.8	1.7	2.8	1.7	0.8	0.5	0.9	0.5
CIS-5	0.5	0.2	-	-	0.1	0.1	2.0	0.8	2.5	1.0	1.2	0.5	1.6	0.6
TRANS-6	1.0	1.0	-	-	-	-	4.0	4.0	3.0	3.0	-	-	-	-
TRANS-7	0.9	0.8	-	-	0.1	0.1	3.5	3.2	2.8	2.5	0.2	0.2	0.2	0.2
TRANS-8	0.8	0.6	-	-	0.1	0.1	3.3	2.6	2.8	2.2	0.4	0.3	0.6	0.5
TRANS-9	0.6	0.4	0.1	0.1	0.1	0.1	2.7	1.6	2.4	1.4	1.1	0.6	1.0	0.6
TRANS-10	0.5	0.2	0.1	0.1	0.1	0.1	2.1	1.0	2.1	1.0	1.5	0.7	1.6	0.7

decomposed (CIS-3, CIS-4, and CIS-5) samples of cis-1,4 polyisoprene. The highlights of the spectrum of CIS-1 are as follows: =CH– methine protons, 4.5 to 5.0 τ (center at 4.75 τ); –CH$_2$– methylene protons, 7.5 to 8.1 τ (center at 7.87 τ); –CH$_3$ methyl protons, 8.1 to 8.5 τ (center at 8.28 τ).

These agree well with those reported in the literature [19-21]. Using these assignments, the apparent (A) and normalized intensities (N) of all peaks in the spectra of undecomposed and decomposed samples of cis polyisoprene were computed. The results are presented in Table 2. Values of A were computed with the assumption that irrespective of the weight-loss the number of protons in a monomer unit of the polymer chain remains constant at 8 and it is only the environment or nature of certain groups that is affected possibly by interchain reactions thereby causing an upfield movement of their protons. In the calculation of N, however, the percent weight loss has been taken into consideration by making the assumption that all types of protons are equally affected by the thermal decomposition of the polymer. The results in Table 2 indicate that on decomposition the peak intensities at 4.75, 7.87, and 8.28 τ decrease, whereas additional peaks appear between 8.5 and 9.5 τ. Furthermore, the apparent as well as the normalized intensities of these new peaks increase with increasing temperature of decomposition. In the case of the decomposed polymers CIS-3, CIS-4, and CIS-5, the percentages of protons located between 8.5 and 9.5 τ were 11, 20, and 35, respectively.

In Fig. 5 are shown the NMR spectra of undecomposed (TRANS-6) and decomposed (TRANS-8, TRANS-9 and TRANS-10) samples of trans-1,4-polyisoprene. The highlights of the spectrum of TRANS-6 are as follows: =CH– methine protons, 4.5 to 5.0 τ (triplet at 4.73, 4.76, 4.79 τ); –CH$_2$– methylene protons, 7.7 to 8.1 τ (pentuplet at 7.82, 7.85, 7.88, 7.91, 7.94 τ); –CH$_3$ methyl protons, 8.2 to 8.6 τ (center at 8.35 τ).

These observations agree well with the assignments reported in the literature [19-21]. Making use of these, the values of A and N for all peaks in the spectra of undecomposed (TRANS-6) and decomposed (TRANS-8, TRANS-9, and TRANS-10) trans-1,4-polyisoprene were computed. The results are also presented in Table 2. These show that on decomposition, the intensities of the peaks centered at 4.76, 7.91 and 8.35 τ decrease whereas additional peaks appear between 8.5 and 9.5 τ. Furthermore, as in the case of cis-1,4-polyisoprene, here as well the values of A and N associated with the new peaks increase with increasing temperature of decomposition.

In the case of the decomposed polymers TRANS-7, TRANS-8, TRANS-9, and TRANS-10, the percentages of protons located beyond 8.5 τ were 5, 12.5, 26, and 38, respectively. Similar observations are also reported in the case of 3,4-polyisoprene where, on treatment with POCl$_3$, the resulting products showed additional peaks in the
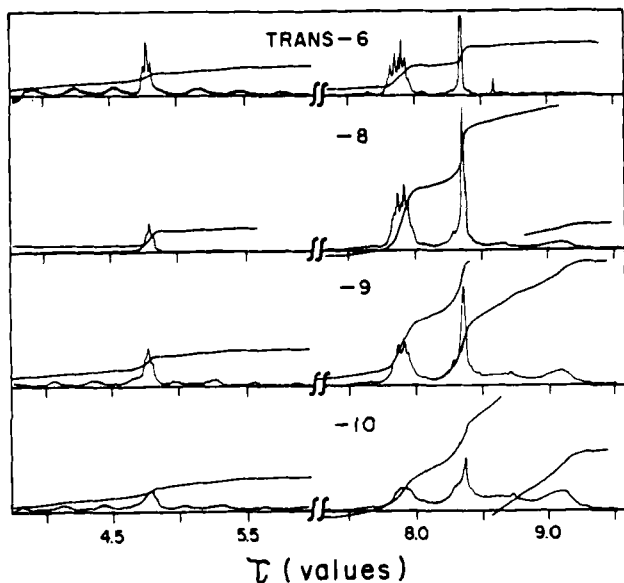
FIG. 5. NMR spectra of undecomposed and decomposed samples of trans-1,4-polyisoprene observed in o-dichlorobenzene at 100°C. (See Table 2 for other data.)

vicinity of 9.0 τ in their NMR analysis [21]. These were attributed to the formation of ladder polymers whose fused cyclohexane rings appear at 9.0 τ. Photoinduced [19] and TiCl$_4$-treated [18] trans- formations of 1,4-polyisoprene and TiCl$_4$ treated-cyclization of 3,4 polyisoprene [20] also yielded additional peaks beyond 9.0 τ. These were attributed to methyls on a saturated carbon (9.04 τ) and cyclo- propyl groups (9.6 and 10.3 τ) in the cyclized products, respectively.

Based on the reported assignments, one may conclude that in the products obtained on thermal decomposition of cis-1,4 and trans-1,4- polyisoprenes cyclic structures containing fused cyclohexane rings and structures carrying methyl groups on saturated carbons are present. Since fused cyclohexane rings appear at a τ value of 9.0 and cyclopropane rings at 9.6 τ and beyond, it is quite possible that in the present study other macrocyclic structures may also exist whose methylene protons appear in the vicinity of 9.3 τ.

Decomposition of PPIPαMS

Detailed studies on the thermal decomposition of PPIPαMS were reported earlier from this laboratory [7]. Based on the GPC
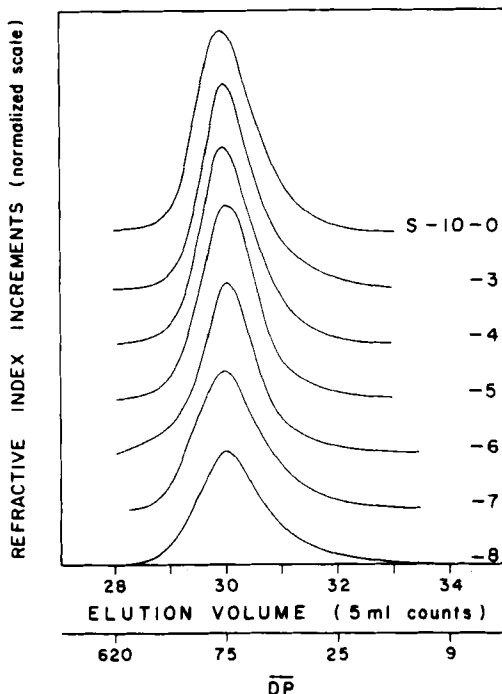
FIG. 6. GPC molecular weight distributions of PPIPαMS sample S-10 subjected to isothermal treatments for 50 min at different temperatures. (See Table 1 for other data.)

molecular weight distribution data it was shown that the process involved in the decomposition was that of depolymerization, where a random proportion of the polymer leaves the reaction medium without affecting the $\overline{M}_w$ and $\overline{M}_n$ molecular weights [23]. In order to demonstrate the molecular weight distribution changes associated with the process of depolymerization, the results on the thermal decomposition of PPIPαMS (sample S-10) at different temperatures were retained for the present studies.

In Fig. 6 are shown the GPC molecular weight distributions of undecomposed (S-10-0) and decomposed (S-10-3 to S-10-8) samples of PPIPαMS. One notes that all of the samples elute at the same maximum elution count of 30 (150 ml). Values of $\overline{M}_w$, $\overline{M}_n$, $\overline{P}_d$, and α (the percent weight loss) obtained both before and after the 50 min
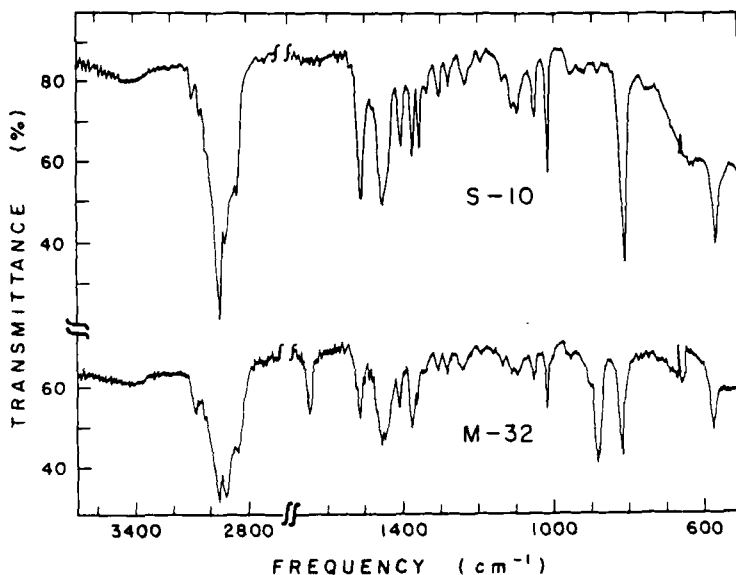
FIG. 7. IR spectra of PPIPαMS sample S-10 and poly(isoprene-PIPαMS) sample M-32 recorded on KBr pellets.

isothermal decompositions are summarized in Table 1. It may be noted that the changes in $\overline{M}_w$ and $\overline{M}_n$, even on decomposition at 300°C where 36% of the polymer disappears from the reaction medium, are not significant. As far as the structural and configurational changes on decomposition are concerned, these also are not very important [7].

Decomposition of Poly(isoprene/PIPαMS)

In Fig. 7 are shown the IR spectra of (PPIPαMS) sample S-10 and that of polymer M-32 prepared from the isoprene and PIPαMS monomers. The spectra of cis- and trans-polyisoprenes were shown earlier in Figs. 2 and 3, respectively. One notes that polymer M-32 has most of the important peaks of (PPIPαMS) and of the polyisoprenes. The peaks at wavenumbers (cm^{-1}) 1650 and 890 in polymer M-32 suggest that the configuration of the isoprene units, in all probability, is a 3,4 addition.

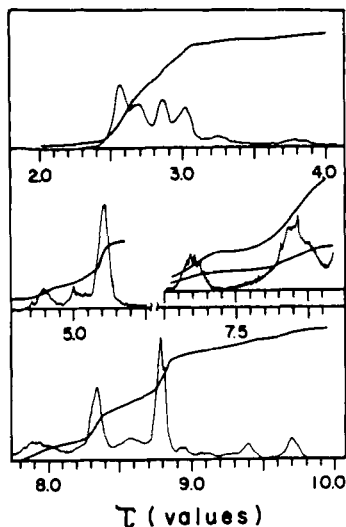In Fig. 8 is shown the NMR spectrum of polymer M-32. The τ

FIG. 8. NMR spectra of polymer sample M-32 observed between 2.0 and 4.0 τ in CCl$_4$ at 75°C and between 4.0 and 10.0 τ in o-dichloro-benzene at 100°C.

value assignments for the various protons in polymer M-32 are as follows: benzene (PPIPαMS), 2.3 to 4.0 τ; =CH– vinylene (cis-1,4 polyisoprene), 4.7 to 4.9 τ (center 4.8 τ); CH$_2$=CH– vinyl (1,2 poly-isoprene), 4.9 to 5.1 τ (center 5.05 τ); CH$_2$=C $\leq$ vinyl (3,4-poly-isoprene), 5.1 to 5.4 τ (center 5.25 τ); –CH– methine (PPIPαMS), 7.0 to 7.4 (septet), –CH$_2$– methylene (cis-1,4-polyisoprene, 1,2-polyisoprene, and 3,4-polyisoprene), 7.4 to 8.1 τ; –CH– methine (3,4-polyisoprene), 7.4 to 8.1 τ; –CH$_2$– methylene (PPIPαMS), 8.1 to 8.6 τ; –CH$_3$ methyl (cis-1,4 polyisoprene), 8.37 τ; –CH$_3$ methyl (3,4-polyisoprene), 8.41 τ; –CH(CH$_3$)$_2$ methyl of isopropyl (PPIPαMS), 8.65 to 8.9 τ (doublet); –CH$_3$ α-methyl (PPIPαMS), 9.0 to 9.8 τ (9.1 mm, 9.4 mr, 9.7 rr).

By making use of these assignments in combination with the integral values of each of the peaks it was established that copolymer M-32 had three isoprene units for every two units of PIPαMS. Furthermore, polyisoprene in polymer M-32 did not have a unique configuration but consisted of a mixture of 3,4-polyisoprene ($\sim$ 60%) (structure IV), 1,2-polyisoprene (10%) (structure V), and 1,4-polyisoprene (30%) (structure VI).

In Fig. 9 are shown the normalized GPC molecular weight
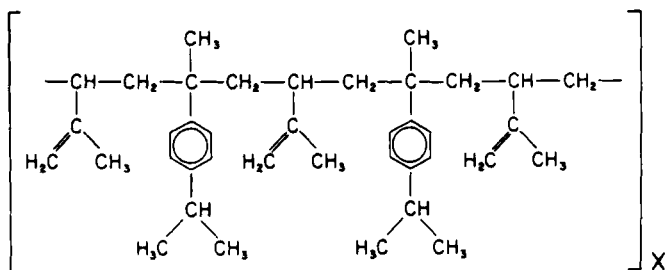
IV
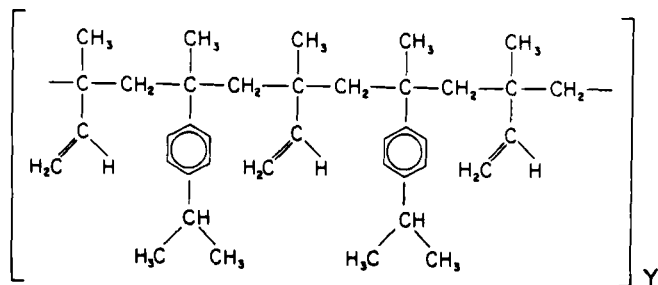
V

distributions of undecomposed (M-32-0) and decomposed (M-32-1 to
M-32-9) samples of poly (isoprene/PIPαMS). The normalizations
of these curves were performed using the decomposition weight-loss
data at the different temperatures presented in Table 3. It may be
noted from Fig. 9 that the intensities of the peaks at elution counts
of 30 and 31.5 decrease with thermal decomposition, whereas
additional broader peaks appear between elution counts 26 and 28
and again between 33 and 35. The overall $\overline{M}_w$ and $\overline{M}_w/\overline{M}_n$ values

of the decomposed polymers (Table 3) increase with increasing
temperature of decomposition. These increases in the values of $\overline{M}_w$
suggest the presence of crosslinking reactions.

In order to obtain a better understanding of this decomposition
process, the normalized GPC molecular weight distributions of the
decomposed polymers (M-32-1 to M-32-9) were successively sub-
tracted from that of the undecomposed polymer M-32-0. This is
shown in Fig. 10, where the GPC molecular weight distributions of
polymers M-32-1, M-32-5, and M-32-9 are compared with that of
M-32-0 and broken down into various components. The volatilized
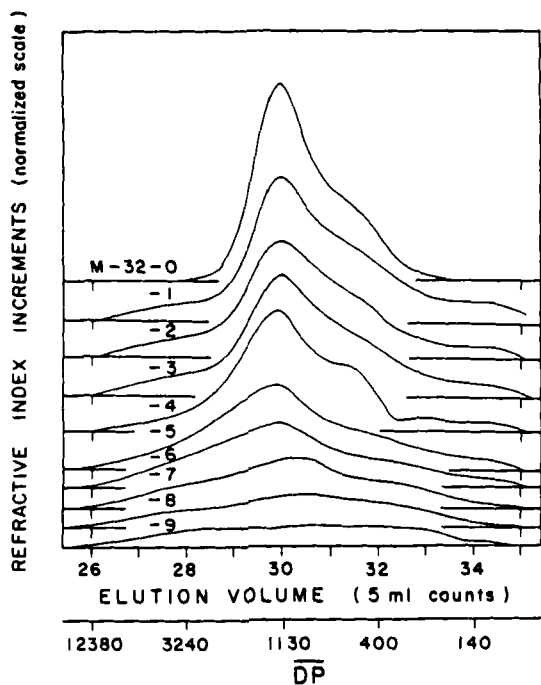fraction of the polymer is represented, in each case, by the area

VI

FIG. 9. GPC molecular weight distributions of polymer M-32
subjected to isothermal treatments for 50 min at different tempera-
tures. (See Table 3 for other data.)

marked with vertical hash lines and the symbol (-) whereas the
higher molecular weight crosslinked as well as the lower molecular
weight surplus polymer is represented with horizontal hash lines
and the symbol (+). Furthermore, these same areas have been con-
verted into distributions shown in the form of dashed lines.

One notes that parts of polymer M-32, eluting between counts 28
and 31.5 and having a maximum at 30 ($\overline{DP}$ = 1130) and between
counts 30 and 33 with a maximum at 31.5 ($\overline{DP}$ = 400), disappear,
whereas others eluting between counts 26 and 30 (with a maximum
at 28, $\overline{DP}$ = 3240) and between counts 32 and 35 (with a maximum
at 34, $\overline{DP}$ = 140) reappear following thermal decomposition. The
complete analyses covering all of the decomposition runs are pre-
sented in Table 3. It should be noted that up to 300°C, decomposi-
tion and cross-linking go hand-in-hand. Beyond 300°C, decomposi-
tion takes over completely and polymer molecules having $\overline{DP}$'s
between 140 and 3240 decompose.

TABLE 3. Thermogravimetric and GPC Data on Undecomposed (M-32-0) and Decomposed (M-32-1 to M-32-9) samples of Poly(isoprene-PIPαMS)

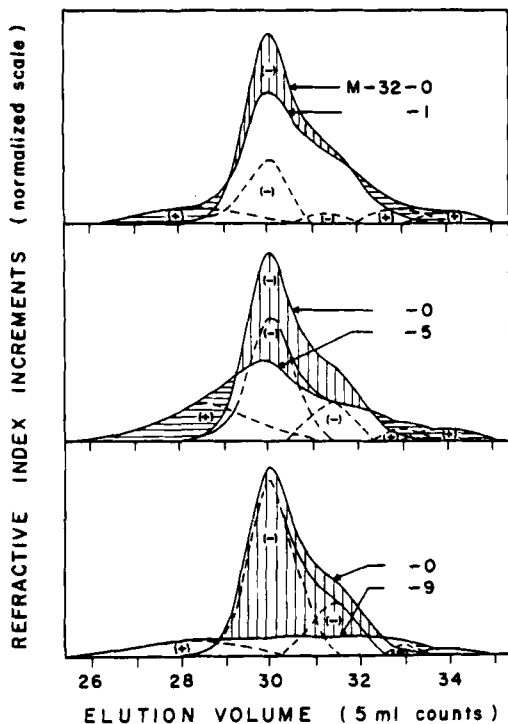| Sample	Decomposition temperature (°C)	α (%)	$\bar{M}_w \times 10^{-3}$ (GPC)	$\bar{P}_d$	Weight of the polymer at various $\overline{DP}$ values			
					$\overline{DP} = 3240$	$\overline{DP} = 1130$	$\overline{DP} = 450$	$\overline{DP} = 140$
M-32-0	25	0	103	1.25	-	7.0	3.0	-
M-32-1	200	2.2	115	1.8	1.1	4.9	2.7	0.9
M-32-2	225	5.3	143	2.2	1.7	4.1	2.6	0.8
M-32-3	250	6.0	136	2.1	1.6	4.2	2.5	0.8
M-32-4	275	11.4	138	1.9	2.0	4.2	2.1	0.6
M-32-5	290	20.3	141	2.0	2.4	2.6	1.8	0.7
M-32-6	300	29.8	185	2.6	2.5	2.2	1.5	0.6
M-32-7	310	42.0	172	2.6	1.9	1.8	1.4	0.5
M-32-8	318	55.0	175	2.9	1.4	1.2	1.3	0.4
M-32-9	325	64.2	216	3.6	1.3	0.7	1.2	0.4

FIG. 10. Graphical method of analysis whereby the GPC molecular weight distribution curves are broken down into components: the case of polymer M-32 subjected to 50 min isothermal treatments at different temperatures. (See Table 3 for other data.)

The GPC molecular weight distributions of the undecomposed and decomposed poly(isoprene/PIPαMS) have the same maxima and resemble those obtained on the decomposition of PPIPαMS where depolymerization has been shown to operate. The presence of small quantities of polymer at elution counts 32 to 35 in M-32-1 to M-32-9, however, does suggest that some random-scissions may also be taking place.

The results of the GPC molecular weight distribution studies on decomposed polymer M-32 have clearly demonstrated the presence of crosslinked products. The mechanism of reactions leading to such structures needs to be explored. Polymer M-32 is a product of the simultaneous polymerization of isoprene with PIPαMS where three units of the former are found associated with two of the latter. In this

polymer, very frequently two units of isoprene are bound to be linked together. In the study of the crosslinking reaction not only does one have the possibility of an isoprene unit cyclizing with a PIPαMS unit but also with another isoprene unit. Furthermore, as the isoprene units in M-32 are not in a unique configutation but exist as cis-1,4-polyisoprene, 1,2-polyisoprene, and 3,4-polyisoprene, numerous other possible ways of cyclization exist and must also be considered.

Cyclization of cis- and trans-1,4-polyisoprene [16, 18, 20] and 3,4-polyisoprene [16, 17, 19, 24] are described in the literature. The mechanism of cyclization involving 1,2-polyisoprene is not known, but it should not be very much different from that of 3,4-polyisoprene. Since the mechanism of cyclization involving 1,4-polyisoprene was discussed earlier, only that of 3,4-polyisoprene has been retained here for discussion.

Polymerization of isoprene with complex catalysts consisting of arylmagnesium bromide or triethylaluminum and excess $TiCl_4$ leading to powdery crosslinked polymers was reported by Gaylord et al. [16]. According to these workers, the initial stage of the polymerization involves 3,4-isotactic or 3,4-syndiotactic polymerization of the trans monomer. A reversal of the direction of polymerization involving intramolecular cyclopolymerization, after the formation of an initial five-membered ring, results in a sequence of fused six-membered rings. Alternatively, the cyclization may be initiated by the copolymerization of a monomer unit or growing chain with the pendant double bond. In the 3,4-isotactic sequence, the structure of cyclopolymer was suggested to be a linear ladder polymer containing fused cyclohexane units whereas in the syndiotactic sequence, spiral ladder polymers were obtained [16].

The cyclization of 3,4-polyisoprene involving carbonium ion attack by one isopropenyl group on another adjacent group was reported by Golub and Heller [19]. Binder [24], who studied the attack of $POCl_3$ on 3,4-polyisoprene, also showed the presence of ladder polymers. The mechanism of reaction leading to ladder polymers [19] is similar in nature to those reported by Stolka et al. [17].

The IR spectra of the H_2SO_4-treated 3,4-polyisoprene [17] rich in ladder polymers showed the following changes as compared to that of the untreated polymer: 1784 cm^{-1} band is absent; 1643 cm^{-1} band shifts to 1650 cm^{-1}; 1450 cm^{-1} band shifts to 1465 cm^{-1}; 1378 cm^{-1} band splits into 1385 cm^{-1} and 1370 cm^{-1}; 1085 cm^{-1} band shifts to 1100 cm^{-1}; 888 cm^{-1} band decreases [19]; and 1265, 1245, 1070, 1040, 1015 cm^{-1} bands appear [19].

The IR spectra of the undecomposed (M-32-0) and decomposed (M-32-6 and M-32-9) samples of polymer M-32 are shown in Fig. 11. Careful study of these spectra reveals the following. (a) The ratio of peak intensities at wavenumbers (cm^{-1}) 2960/(2925 and 2850) corresponding to the stretching vibration of $-CH_3$ and $-CH_2-$ varies from
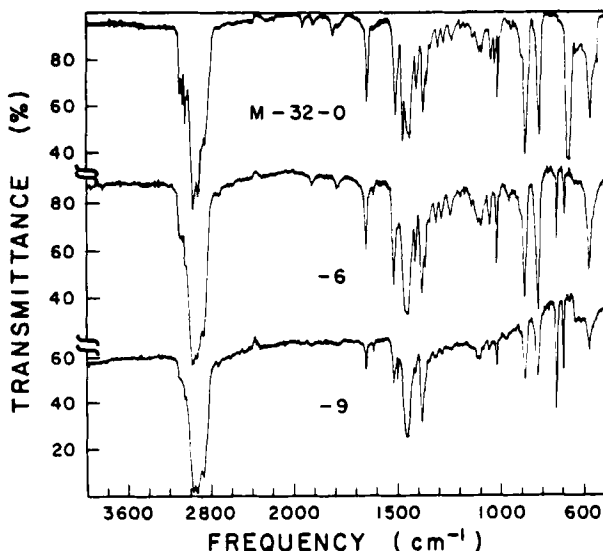
FIG. 11. IR spectra of undecomposed and decomposed samples of polymer M-32. (See Table 3 for other data.)

0.62 (M-32-0) to 0.55 in (M-32-6) to 0.52 in (M-32-9) showing a decrease in –CH$_3$ or increase in –CH$_2$– groups or both. (b) The ratio of the peak intensities at wavenumbers (cm^{-1}) 1650/(2925 and 2850) decreased from 0.28 in (M-32-0) to 0.21 in (M-32-6) to 0.11 in (M-39-9). (c) The ratio of the peak intensities at wavenumbers (cm^{-1}) 890/(2925 and 2850) decreased from 0.44 (M-32-0) to 0.33 in (M-32-6) to 0.23 in (M-32-9).

These IR changes on decomposition suggest that the isopropenyl group of 3,4-polyisoprene is actively involved in the crosslinking reaction. The decrease in the CH$_3$ intensity and an increase in that of –CH$_2$– would suggest that in the crosslinks formed between the isoprene and the PIPαMS units, an α-CH$_3$ or isopropyl CH$_3$ may be involved. It may be added here that crosslinking between two isoprene units on the other hand would increase –CH$_3$ and lower –CH$_2$– linkages. The presence of these latter reactions cannot be confirmed from the IR spectra in Fig. 11; however, if these were present, it would suggest that a large proportion of –CH$_3$ groups of the PIPαMS units are involved in crosslinking. The decrease in the number of double bonds and the involvement of isopropenyl groups in the cross-linking reactions in polymer M-32 are in line with the observations made during the cyclization of 3,4-polyisoprene [17, 19, 24] itself.
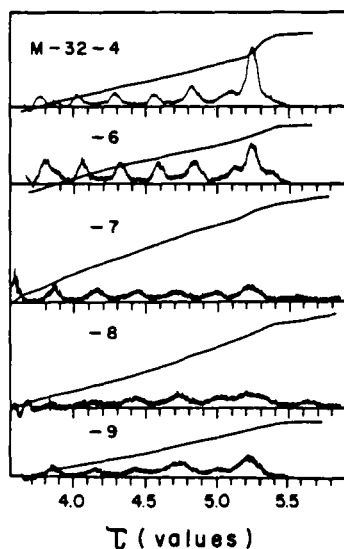
FIG. 12. NMR spectra of decomposed samples of polymer M-32 observed between 3.5 and 5.8 τ in o-dichlorobenzene at 100°C. (See Table 4 for other data.)

In Fig. 12 are shown the NMR spectra of decomposed (M-32-4 to M-32-9) samples of polymer M-32 observed at 100°C in o-dichlorobenzene between 3.5 to 5.8 τ. Although there were only three important peaks at 4.8, 5.05 and 5.25 τ in the NMR spectrum of the undecomposed polymer (Fig. 8), after decomposition there are a few additional peaks between 3.7 and 4.5 τ. Furthermore, the intensity of the peak at 5.25, attributed to $CH_2=$ in 3,4 polyisoprene, has decreased considerably.

The analysis data of the NMR spectra shown in Fig. 12 in terms of the apparent (A) and normalized (N) intensities associated with various important peaks are presented in Table 4. The values of A were computed with the assumption that, irrespective of the weight loss, the number of protons appearing between 3.7 and 5.8 τ remains constant at 5.3 (i. e., 9.4% of the 56 protons in the comonomers), and it is only the environment or nature of certain groups that is affected possibly by inter- or intrachain reactions thereby causing an upfield or downfield movement of their protons. In the calculation of N, however, the weight losses were taken into consideration, and the assumption that all types of protons are equally susceptible to change because of thermal decomposition was invoked.

TABLE 4. Apparent (A) and Normalized (N) Proton Distribution between 3.7 and 6.0 τ for Undecomposed (M-32-0) and Decomposed (M-32-4 to M-32-9) Polymer Samples

Sample	3.7-4.0 τ		4.0-4.25 τ		4.25-4.55 τ		4.55-4.85 τ		4.85-5.05 τ		5.05-5.35 τ		5.35-5.6 τ	
	A	N	A	N	A	N	A	N	A	N	A	N	A	N
M-32-0	-	-	-	-	-	-	0.9	0.9	0.9	0.9	3.5	3.5	-	-
M-32-4	0.6	0.6	0.5	0.5	0.6	0.5	1.3	1.2	0.5	0.5	1.7	1.5	-	-
M-32-6	0.8	0.6	0.7	0.5	0.7	0.5	1.4	1.0	0.5	0.3	1.1	0.8	-	-
M-32-7	0.9	0.5	0.9	0.5	0.8	0.6	0.8	0.6	0.5	0.3	1.0	0.6	0.4	0.2
M-32-8	0.7	0.3	0.7	0.3	0.7	0.3	0.8	0.4	0.7	0.3	1.1	0.5	0.5	0.3
M-32-9	1.1	0.4	0.7	0.3	0.7	0.3	1.2	0.4	0.4	0.2	0.7	0.3	0.4	0.2

The results in Table 4 clearly show that polymer M-32-4 which underwent but an 11.4% weight loss on decomposition at 275°C, has about 50% of its protons appearing between 4.85 and 5.05 τ (CH$_2$=CH– of 1,2-polyisoprene) and between 5.05 and 5.35 τ (CH$_2$= of 3,4-polyisoprene) relocated between 3.7 and 4.7 τ. The downfield movement of the vinyl protons of 1,2-polyisoprene and 3,4-polyisoprene indicate that their nature or environment has been affected. In other copolymers, M-32-6 to M-32-9, which are decomposed products obtained following treatment at 300 and 325°C, the trends are identical in the sense that the intensities of the protons between 4.85 and 5.05 τ and 5.05 and 5.35 τ decrease regularly and these are consistently rearranging themselves, thus appearing elsewhere downfield (3.7 to 4.7 τ) or upfield (5.35 to 5.6 τ). The observation that the double-bonded methylenes of 1,2-polyisoprene and 3,4-polyisoprene are actively involved in the crosslinking reactions agrees well with the IR data discussed earlier.

In Fig. 13 are shown the NMR spectra of the decomposed (M-32-4 to M-32-9) samples of copolymer M-32, observed at 100°C in o-dichlorobenzene between 7.0 and 10.0 τ. The analysis data from these spectra, in terms of apparent and normalized intensities associated with different peaks, are presented in Table 5. In the calculation of the apparent intensities, the total number of protons which appear between 7.0 and 10.0 τ have been kept fixed at 42.7 (i. e., 76% of the 56 protons in the comonomers).

A comparison of the apparent intensities of the undecomposed and decomposed samples of polymer M-32 (Table 5) revealed the following. (a) The intensity between 7.0 and 7.4 τ, attributed to the methine protons in the CH(CH$_3$)$_2$ isopropyl units in M-32, decreases. (b) The intensity between 7.4 and 8.1 τ attributed to the (–CH–) methine protons of 3,4 polyisoprene as well as the (–CH$_2$–) methylene protons of cis-1,4-polyisoprene, 1,2-polyisoprene, and 3,4-polyisoprene decreases initially then remains constant thereafter. (d) The intensity between 8.65 and 8.9 τ attributed to the methyl protons of CH(CH$_3$)$_2$ in the PIPαMS units decreases. (e) The intensity between 8.9 and 9.0 τ attributed to the methyls of the 1,2-polyisoprene as well as to the presence of ladder polymers [19, 20, 24] increases. . (f) The intensity between 9.0 and 9.9 τ attributed to the α-methyl protons of PIPαMS units decreases.

Based on the analyses of Figs. 11, 12, and 13 coupled with the assignment of the 8.9 to 9.0 τ band to ladder polymers [19, 20, 24], it can be said that the CH$_2$=CH– group of 1,2-polyisoprene and the CH$_2$= group of 3,4-polyisoprene are the active centers for the formation of cyclic products. Furthermore, the α-CH$_3$ as well as the methyls of the isopropyl groups in the PIPαMS monomer are also involved in the cyclization process. Based on skeletal structures IV to VI, it would be safe to conclude that although the isoprene units
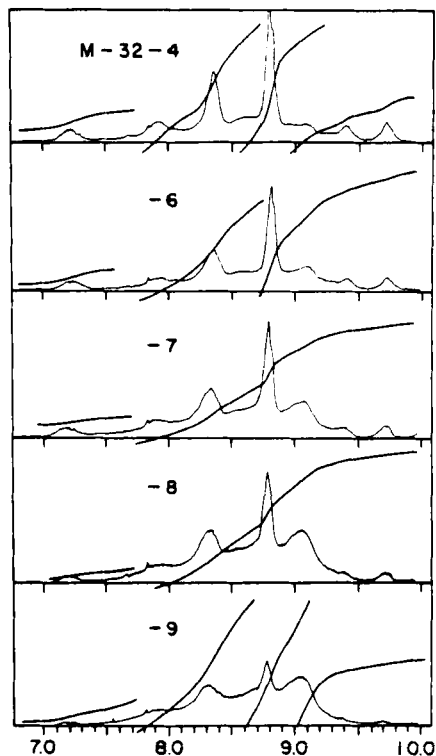

FIG. 13. NMR spectra of decomposed samples of polymer M-32 observed between 7.0 and 1.0 τ in o-dichlorobenzene at 100°C. (See Table 5 for other data.)

can be involved in inter (isoprene to isoprene) chain cyclization as well as intrachain (isoprene with PIPαMS) cross-linking. The PIPαMS units take part in only the latter reaction. In the event that α-CH₃ groups of PIPαMS are involved in interchain cyclization, the isoprene units would have to be in the trans configuration to be able to cyclize. In the case of isoprene to isoprene interchain cyclization, the configuration in which these two units would be present is difficult to assess.

In Fig. 14 are shown the dynamic thermogravimetric curves for polymers S-10, CIS-1, TRANS-6, and M-32, respectively. By using the method of Coats and Redfern [28, 29], activation energies were calculated for zero- and first-order kinetics. These results are

TABLE 5. Apparent (A) and Normalized (N) Proton Distribution between 7.0 and 10.0 τ for the Undecomposed (M-32-0) and Decomposed (M-32-4 to M-32-9) Polymer Samples

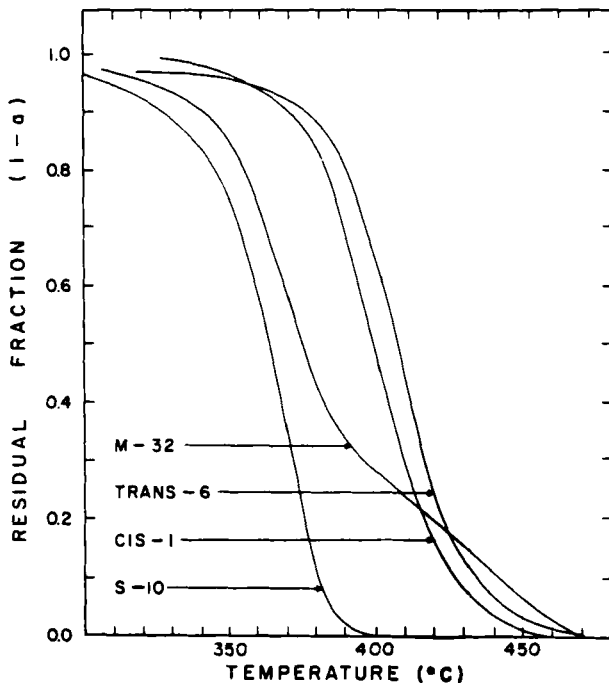| Sample	7.0-7.4 τ		7.4-8.1 τ		8.1-8.65 τ		8.65-8.9 τ		8.9-9.0 τ		9.0-9.9 τ	
	A	N	A	N	A	N	A	N	A	N	A	N
M-32-0	2.0	2.0	8.8	8.8	9.7	9.7	11.3	11.3	4.5	4.5	6.3	6.3
M-32-4	2.0	1.8	6.0	5.3	12.3	10.9	12.0	10.6	5.0	4.4	5.7	5.0
M-32-6	2.1	1.5	5.4	3.8	11.6	8.1	11.5	8.1	6.3	4.5	6.1	4.3
M-32-7	1.5	0.9	6.6	3.8	12.5	7.3	10.6	6.2	7.8	4.5	4.0	2.3
M-32-8	1.4	0.6	6.1	2.7	12.4	5.6	9.5	4.3	9.1	4.1	4.3	1.9
M-32-9	1.5	0.5	6.5	2.4	12.8	4.6	9.2	3.3	11.1	4.0	1.6	0.6

FIG. 14. Dynamic thermogravimetric decomposition of polymer samples S-10, CIS-1, TRANS-6, and M-32 heated at a rate of 20°C/min. (See Table 6 for other data.)

presented in Table 6. The activation energy values for cis- (53.9 kcal/mole) and trans- 1,4-polyisoprene (50.9 kcal/mole) for first-order kinetics are not far from the 56-63 kcal/mole values reported for these polymers in the literature [1]. The difference in the values for cis- and trans-1,4-isoprene arises, in all probability, from the difference in their $\overline{M}_n$ values. For an $\overline{M}_n$ of about 82×10^3, the extrapolated activation energy for polyisoprenes would be ~ 48.5 kcal/mole, which is of the same order of magnitude as that for PPIPαMS sample F-5 (50.9 kcal/mole). The activation energy in the case of poly(isoprene/PIPαMS) for first-order kinetics is 43.7 kcal/mole when $\alpha < 0.6$ and 9.3 kcal/mole when $\alpha > 0.6$. Though the activation energy value when $\alpha < 0.6$ is lower but not too far removed from the corresponding values for polyisoprene and PPIPαMS, the value when $\alpha > 0.6$ shows a considerable decrease. It would appear that at α values above 0.6 reactions other than crosslinking and de-polymerization are operative.

TABLE 6. Activation Energy Values for the Decomposition of Poly-isoprene, PPIPαMS and Poly(isoprene-PIPαMS)

Sample	Molecular weight $\overline{M}_n \times 10^{-3}$	Activation energy (kcal/mole)	
		For n = 0[a]	For n = 1[a]
S-10[b]	10	30.0	-
F-5[b]	70	-	50.9
S-25[b]	130	30.2	43.5
CIS-1	672	-	53.9
TRANS-6	304	-	50.9
M-32			
a < 0.6	82	37.3	43.7
a > 0.6		2.5	9.3

[a] n is the order of reaction.
[b] Data from Malhotra et al. [7].

The principal conclusions to be drawn from this study may be summed up as follows. (a) The thermal decompositions of cis- and trans-1,4 polyisoprene proceed via a random-scission mechanism which follows first-order kinetics. IR and NMR analyses show the presence of cyclic products in the decomposed polymers, due, quite possibly, to interchain crosslinking. (b) The thermal decomposition of PPIPαMS involves a depolymerization process which also follows first-order kinetics. (c) The thermal decomposition of poly(isoprene/PIPαMS) proceeds via a depolymerization process. Inter- as well as intrachain reactions yield cyclic and crosslinked polymers. The active centers for these cyclization reactions are at the double-bonded methylenes of 3,4- and 1,2-polyisoprene. The isopropyl methyls and α-methyls are also involved in crosslinking reactions. The isoprene units are active in inter (isoprene to isoprene) cycliza-tion as well as intra (isoprene to PIPαMS) crosslinking, however, the PIPαMS units take part in only the latter reaction. The overall reaction obeys first-order kinetics. The activation energy for decom-positions where α < 0.6 in polymer M-32 is of the same magnitude as that for the decomposition of polyisoprene and PPIPαMS but at α values > 0.6, the energy of activation decreases considerably, indicating that reactions other than crosslinking and depolymerization are most likely taking part.

Decomposition studies involving substituted styrenes are in progress and will be reported in due course.

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