Polymers from Renewable Resources. VIII. Thermal Properties of the Interpenetrating Polymer Networks Derived from Castor Oil–Isophorone Diisocyanate–Polyacrylamides

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SYNOPSIS

Castor oil was reacted with isophorone diisocyanate varying the isocyanate/hydroxyl ratio to produce a number of polyurethanes (PUs). All the PUs were reacted with acrylamide and methacrylamide using ethylene glycol dimethacrylate as the crosslinker and benzoyl peroxide as the initiator. Thermogravimetric analysis of the polymers was conducted using a computer analysis method for assigning the kinetic mechanism. The degradation steps have been discussed in the light of the kinetic parameters. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Recently, the use of renewable resources has gained considerable importance as a potential source of energy and an alternative energy source to the ever-receding fossil-based derivatives. With the petroleum stocks facing exhaustion day-by-day, modern methods and means have to be devised to meet the challenges to the needs of modern civilization. This can be fulfilled only by switching over to alternative natural energy sources based on agricultural products to meet the requirements for carbon-based monomers for the polymer industry in the 21st century.

Over the years, a number of triglyceride oils,[1,2] such as castor,[3,4] lesquerella,[3] and vernonia oils,[5,6] have been used by Sperling et al.[7–17] to prepare a large number of interpenetrating polymer networks (IPNs). These oils contain the hydroxyl group as well as the unconjugated vinyl group in the backbone. The hydroxyl group could be used for step-growth polymerization to form elastomeric materials and the vinyl group could be used

through a chain-growth mechanism to form polymerized plastics. Therefore, the elasticity and plasticity could be controlled in a single backbone chain to produce a number of IPNs for the required end uses.

Recently, we reported the synthesis and characterization of some IPNs from castor oil using a multitude of vinyl monomers.[18–20] This communication presents the thermal properties of IPNs prepared from castor oil–isophorone diisocyanate and acrylamide and methacrylamide as monomers. The thermal properties of the IPNs were studied by using a novel LOTUS package method developed by Rao and Mohanty.[21] This method provides opportunities for the calculation of the energy of decomposition in different segments of the thermogravimetric curve.

During the last several years, different methods have been used for evaluating kinetic parameters from thermogravimetric (TG) analysis measurements. Sbirrazzuoli et al.[22] discussed the validity and application of different methods. Zsako[23] developed a method based on the standard deviation which deals mainly with a comparison of $-\log p(x)$ values at different temperatures and activation energies with $\log g(\alpha)$ and assigns the mechanism for the data with the minimum standard deviation. Al-

though this method is fairly exhaustive, it is tedious to use.

Satava and Skvara[24] developed a graphical method for comparison of log $g(\alpha)$ with log $p(x)$. This method is based on the principle of the rate of decomposition expressed as

$$d\alpha/dt = kf(\alpha) \qquad (1)$$

where $f(\alpha)$ depends on the mechanism and k is the rate constant. The temperature dependence is given by the Arrhenius equation

$$k = Z \exp(-E/RT) \qquad (2)$$

where Z is the statistical frequency factor, and E, the activation energy. Because thermogravimetric analysis is carried out at constant temperature,

$$q = dT/dt \qquad (3)$$

Combining eqs. (1)–(3),

$$d\alpha/f(\alpha) = Z/q \exp(-E/RT) \, dt \qquad (4)$$

Integration of this equation results in the TG curve.[25]

The analytical form of the function $f(\alpha)$ depends on the mechanism of the thermal decomposition. The most general form of this equation is expressed as

$$f(\alpha) = \alpha^a(1 - \alpha)^b \qquad (5)$$

where a and b are constants called homogeneity factors.

When the analytical function of $f(\alpha)$ is known, this leads to new function $g(\alpha)$. For a known activation energy, Doyle[25] derived the relationship obtained by integration of eq. (4):

$$g(\alpha) = \frac{ZE}{Rq} p(x) \qquad (6)$$

and the function $p(x)$ is given by

$$p(x) = \frac{e^{-x}}{x} - \int_{\phi}^{\alpha} \frac{e^{-u}}{u} \, du \qquad (7)$$

where $u = E/RT$ and $x = E/RT_\infty$. This function has been tabulated by Zsako[23] for different temperatures and activation energies. The logarithmic form of eq. (6) is

$$\log(ZE/Rq) = \log g(\alpha) - \log p(x) = \beta \qquad (8)$$

where β is independent of temperature. This procedure has led to a simpler application of regression analysis between $\log g(\alpha)$ and reciprocal temperature and assigns the kinetic mechanism to the model with a regression value R^2 close to unity.

All these procedures have a number of sequential calculations which have proved to be cumbersome and have resulted in the use of computers in this field. Several packages[26-31] have been developed, mainly using either FORTRAN or BASIC compilers, for the determination of the kinetic mechanism of decomposition. Essentially, all these packages are restricted by fixing the preexponential factor, activation energy, correlation index, etc. Although graphic representation is widely acceptable for the presentation of analysis, these packages lack this ability. Hence, the need for development of a new package is obvious.

Recently, Rao and Mohanty[21] developed a new computer analysis method for the evaluation of the kinetic parameters of the decomposition of solids. Spreadsheets with built-in graphics capabilities have been found to be the most suitable for this TG analysis. To illustrate the capabilities of the spreadsheets, LOTUS-123 was chosen for analysis of TG data. This package uses the procedure suggested by Nair and Madhu Sundrar[26] which uses regression analysis. The program was written using LOTUS-MACROS for analysis of the nine kinetic models given in Table I.

Based on this spreadsheet analysis, a package for determining the kinetic mechanism in a nonisothermal process has been developed. Necessary cell relationships have been used to evaluate different log $g(\alpha)$ functions for different temperatures. Regression analysis is carried out for $1/T$ and log $g(\alpha)$. The regression value is given by

$$R^2 = \frac{(XY - n\bar{X}\bar{Y})^2}{(X^2 - n\bar{X}^2)(Y^2 - n\bar{Y}^2)} \qquad (9)$$

The slope is given by

$$b = \frac{XY - n\bar{X}\bar{Y}}{X^2 - n\bar{X}^2} \qquad (10)$$

and the constant is given by

$$a = \bar{Y} - b\bar{X} \qquad (11)$$

Table I Kinetic Functions (Integral Differential Forms) Used for the Data Analysis

Function	Name of Function	$g(\alpha)$	$f(\alpha)$	Rate-controlling Process
D_1	Parabolic law	α^2	$1/(2\alpha)$	One-dimensional diffusion
D_2	Valensi (Barrer) equation	$\alpha + (1 - \alpha)\ln(1 - \alpha)$	$[-\ln(1 - \alpha)]^{-1}$	Two-dimensional diffusion, cylindrical symmetry
D_3	Jander equation	$[1 - (1 - \alpha)^{1/3}]^2$	$\frac{3}{2}(1 - \alpha)^{2/3} \times [1 - (1 - \alpha)^{1/3}]^{-1}$	Three-dimensional diffusion, spherical symmetry
D_4	Ginstling–Bruonshtein equation	$(1 - \frac{2}{3}\alpha) - (1 - \alpha)^{2/3}$	$\frac{3}{2}[(1 - \alpha)^{-1/3} - 1]^{-1}$	Three-dimensional diffusion, spherical symmetry, reaction starting on exterior
F_1	Avrami–Erofeev equation ($n = 1$)	$-\ln(1 - \alpha)$	$(1 - \alpha)$	Assumes random nucleation, one nucleus, one particle
A_2	Avrami–Erofeev equation ($n = 2$)	$[-\ln(1 - \alpha)]^{1/2}$	$2(1 - \alpha) \times [-\ln(1 - \alpha)]^{1/2}$	Assumes random nucleation and its subsequent growth
A_3	Avrami–Erofeev equation ($n = 3$)	$[-\ln(1 - \alpha)]^{1/3}$	$3(1 - \alpha) \times [1 - \ln(1 - \alpha)]^{2/3}$	Assumes random nucleation and its subsequent growth
R_2	Contracting cylinder	$1 - (1 - \alpha)^{1/2}$	$2(1 - \alpha)^{1/2}$	Phase-boundary reaction, cylindrical symmetry
R_3	Contracting sphere	$1 - (1 - \alpha)^{1/3}$	$3(1 - \alpha)^{2/3}$	Phase-boundary reaction, spherical symmetry

where $X = 1/T$ and $Y = \log g(\alpha)$, and n is the number of observations. The mechanism which has R^2 closest to unity is chosen.

The program deals mainly with data entry: The temperature range in °C, the rate of heating q, and the α values. The program evaluates the values for $\log g(\alpha)$ and $1/T$ and carries out regression analysis for $1/T$ vs. $\log g(\alpha)$. It saves the results of slopes, constants, and R^2 values corresponding to each mechanism and also plots the graphs for each of the mechanisms and prints out the results.

Based on the computer analysis method, the various kinetic parameters for the degradation of the IPNs listed in Table II were calculated and are listed in Tables III and IV.

EXPERIMENTAL

Materials

Castor oil (refined) was used without any purification. It was obtained from the local market. Its characteristic values such as hydroxyl number, acid number, and isocyanate equivalent were determined by standard procedures.[18]

The chemicals used in the investigation were of analytic grade. Benzoyl peroxide was recrystallized from chloroform and vinyl monomer was freed from inhibitor before use. The isocyanate content was determined by titration with standard n-butylamine with accuracy.

Polyurethane Synthesis

Castor oil (10.11 g, 0.0108 mol) was reacted with isophorone diisocyanate (IPDI) (4.817 g, 0.0218 mol) to maintain the NCO/OH ratio at 1.6. The reaction was carried out at 45°C with continuous stirring for 2 h. The prepolymer was isolated as a viscous liquid. Following this procedure, other polyurethanes (PUs) with varing NCO/OH ratios were prepared and also with differing with diisocyanates. Some of these materials were discussed elsewhere.[18]

Table II Chemical Composition and Thermal Decomposition Data of IPNs

Sample	System[a]	Ratio NCO/OH	Composition PU/AM or MAM	% Wt Loss up to Various Temperatures (°C) 100–300	300–400	400–500	OI[b]
IPN$_2$	CO + IPDI + AM	1.6	35 : 65	14	47	90	0.1800
IPN$_5$	CO + IPDI + AM	1.8	35 : 65	14	49	90	0.1800
IPN$_8$	CO + IPDI + AM	2.0	35 : 65	12	44	92	0.1785
IPN$_{11}$	CO + IPDI + MAM	1.6	35 : 65	08	53	98	0.1763
IPN$_{14}$	CO + IPDI + MAM	1.8	35 : 65	17	48	94	0.1775
IPN$_{16}$	CO + IPDI + MAM	2.0	25 : 75	18	42	94	0.1777
IPN$_{17}$	CO + IPDI + MAM	2.0	35 : 65	15	42	94	0.1784

[a] CO = castor oil; IPDI = isophorone diisocyanate; AM = acrylamide; MAM = methacrylamide.
[b] OI = oxygen index.

Synthesis of IPNs

IPNs were synthesized by charging the PU in different proportions into a round-bottom flask. To

Table III Kinetic Parameters of the IPN-14

$g(\alpha)$	Temperature Range (°C)	E (kJ/mol)	R^2
D_1	210–310	41.90	0.9540
D_2	210–310	44.90	0.9586
D_3	210–310	48.30	0.9612
D_4	210–310	46.00	0.9597
F_1	210–310	24.00	0.9561
A_2	210–310	10.20	0.9399
A_3	210–310	5.60	0.9134
R_2	210–310	21.40	0.9533
R_3	210–310	22.30	0.9548
D_1	320–440	75.70	0.9442
D_2	320–440	81.30	0.9569
D_3	320–440	88.20	0.9673
D_4	320–440	83.60	0.9610
F_1	320–440	45.50	0.9704
A_2	320–440	20.50	0.9635
A_3	320–440	12.20	0.9541
R_2	320–440	40.20	0.9585
R_3	320–440	41.90	0.9637
D_1	450–500	77.80	0.9170
D_2	450–500	102.10	0.9395
D_3	450–500	140.90	0.9635
D_4	450–500	114.50	0.9494
F_1	450–500	90.60	0.9752
A_2	450–500	42.70	0.9722
A_3	450–500	26.80	0.9685
R_2	450–500	58.40	0.9505
R_3	450–500	67.90	0.9608

this, the mixture of acrylamide, 1% EGDM, and 0.5% benzoyl peroxide was added. The mixture was stirred at room temperature for 15 min to form a homogeneous solution. The temperature was then increased to 60°C to initiate acrylamide polymerization. After stirring for 1 h, the solution was poured into a glass mold kept in a preheated oven maintained at 60°C. It was kept at this temperature for 24 h and at 120°C for 4 h. The IPN thus formed was cooled slowly and removed from the mold with

Table IV Values of Energy of Activation of Different IPNs Prepared from Castor Oil-based PU–Polyacrylamides

Sample Code	$g(\alpha)$	Temperature Range (°C)	E (kJ/mol)	R^2
IPN-2	F_1	150–230	26.20	0.9449
	F_1	240–420	37.90	0.9488
	F_1	430–480	109.90	0.9636
IPN-5	D_3	140–290	16.60	0.9675
	F_1	300–410	105.10	0.9863
	F_1	420–470	95.00	0.9999
IPN-8	F_1	110–200	24.00	0.9308
	F_1	310–380	32.90	0.9878
	F_1	390–490	65.80	0.9444
IPN-11	D_1	170–420	39.80	0.9699
	F_1	430–490	116.10	0.9804
IPN-16	F_1	80–190	11.00	0.9311
	F_1	200–310	34.10	0.9727
	D_3	320–440	85.10	0.9904
	F_1	450–520	55.20	0.9705
IPN-17	D_3	210–340	61.90	0.9718
	F_1	350–440	63.50	0.9904

different compositions of the same vinyl monomer and PU. Here, we prepared two sets of IPNs taking acrylamide and methacrylamide as the monomers.

RESULTS AND DISCUSSION

From Figures 1–4, it is evident that all the IPNs prepared from castor oil (CO), isophorone diisocyanate (IPDI), acrylamide (AM), and methacrylamide (MAM) exhibit a weight loss of 15% in the temperature range 0–300°C. All the IPNs decompose around 50% in the temperature range 300–400°C and 92–98% in the range 400–500°C. The initial, slow weight loss around 200°C is attributed to the moisture retained in the samples. The weight loss of about 50% between 300 and 400°C may be attributed to the de-crosslinking of IPNs. It is pertinent to mention here that the IPNs contain two or more polymers each in network form. The de-crosslinking occurs between the two network forms in the range 300–400°C. In these types of polymers, one of the polymer networks has been formed or polymerized or crosslinked in the immediate presence of the other. Initially, the PUs are formed by the reaction of diisocyanates with the hydroxyl

groups of ricinoleic acid present in castor oil. This prepolymer (PU) reacts with the vinyl monomer acrylamide or methacrylamide in the presence of a free-radical initiator, benzoyl peroxide, and a cross-linker, ethylene glycol dimethacrylate (EGDM), to form the IPNs having two polymer systems: (i) PU, a condensation polymerization, and (ii) acrylamide with a free-radical initiator. Because the castor oil possesses double bonds, it will probably react to some extent with the acrylamide. From the thermogram, it is evident that there is a sharp decrease in weight loss at around 410°C. This is probably due to de-crosslinking of the network forms of the IPNs. A third weight loss occurs in the range 400–500°C, indicating the complete decomposition of the IPNs at around 500°C. The final weight loss occurs because of the breakage of the bond of the polymer consisting of the polyacrylamide or polymethacrylamide attached to the ricinoleic acid backbone of castor oil.

The results indicate that, for all the polymers, the activation energy values are considerably higher in the temperature range 300–400°C than in range 410–500°C. This clearly indicates that the degradation process is slower at 300–400°C and faster at 410–500°C. This is obvious from the structure of the IPNs. As mentioned earlier, the de-crosslinking between the two types of polymers occurs in the
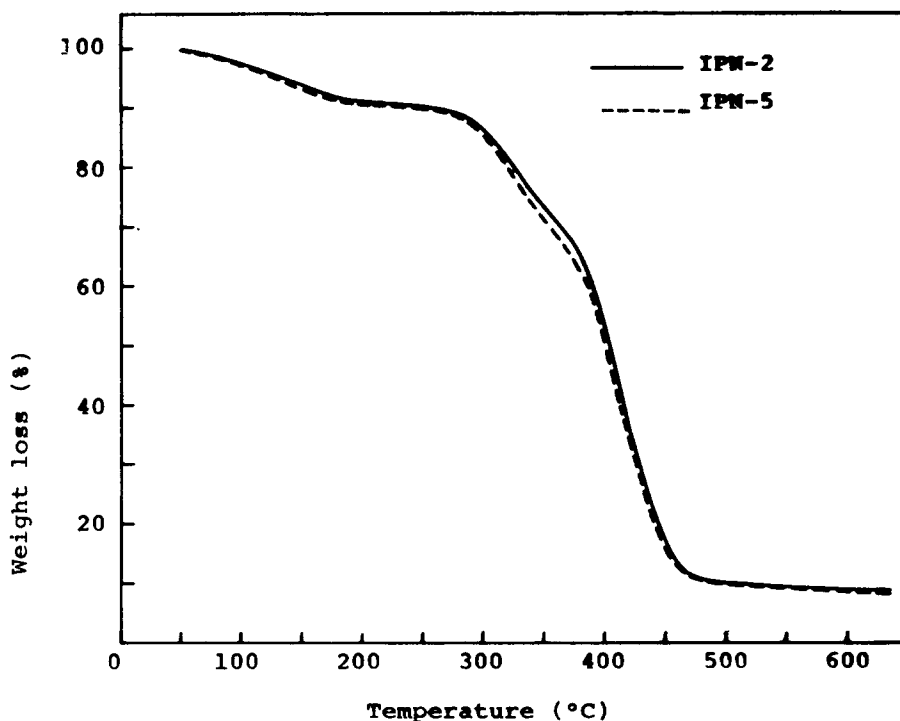

Figure 1   Weight loss curves of the IPNs: (———) CO + IPDI + AM (NCO : OH, 1.6), (PU : AM, 35 : 65); (- - - -) CO + IPDI + AM (NCO : OH, 1.8), (PU : AM, 35 : 65).
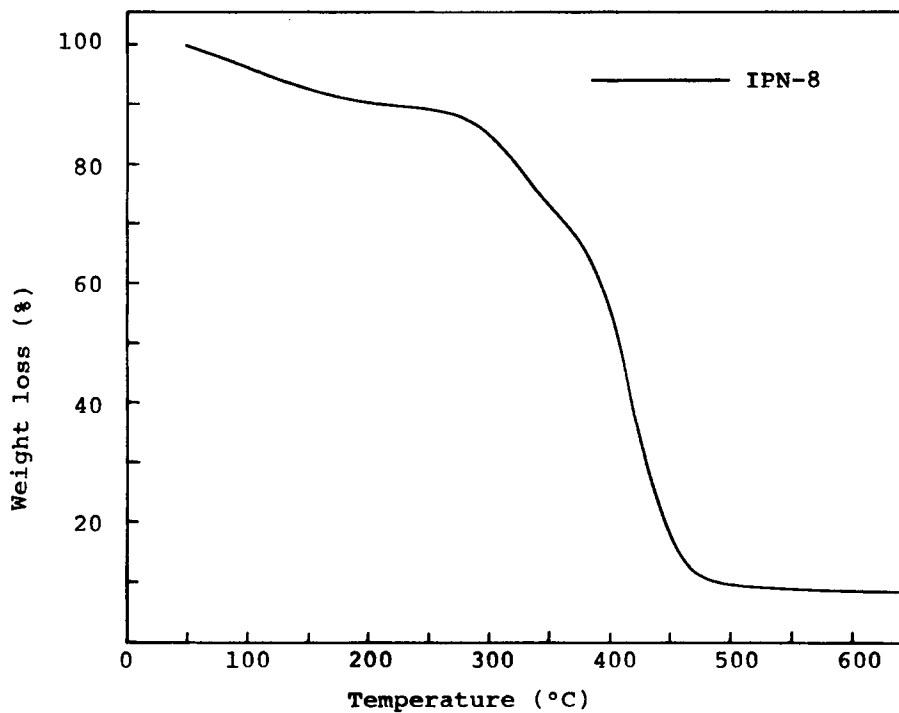
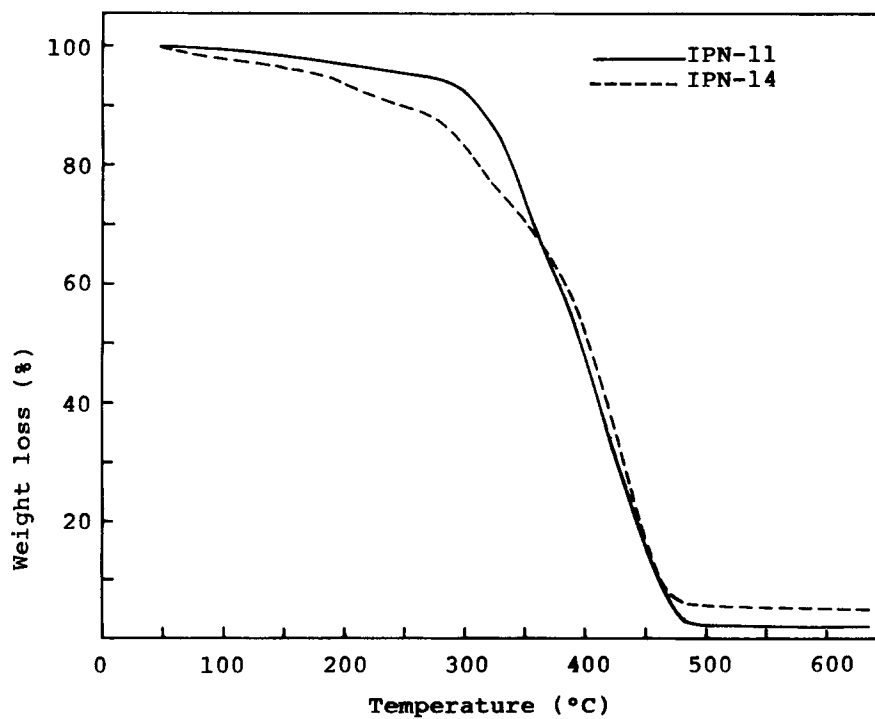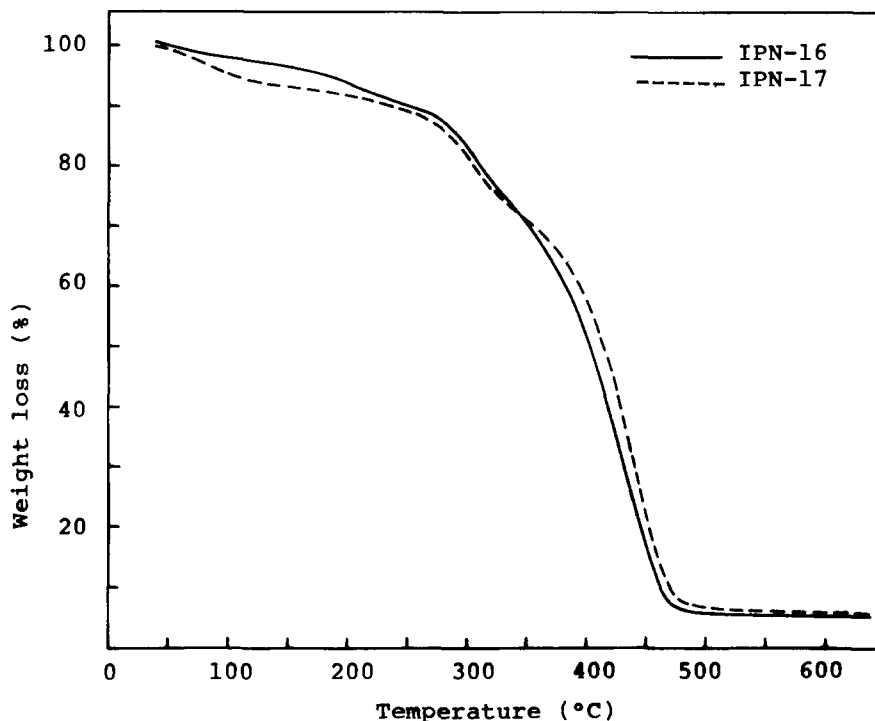**Figure 2** Weight loss curve of the IPNs: (———) CO + IPDI + AM (NCO : OH, 2.0), (PU : AM, 35 : 65).

Figure 3 Weight loss curves of the IPNs: (———) CO + IPDI + MAM (NCO : OH, 1.6), (PU : MAM, 35 : 65); (- - - -) CO + IPDI + MAM (NCO : OH, 1.8), (PU : MAM, 35 : 65).

Figure 4   Weight loss curves of the IPNs: (———) CO + IPDI + MAM (NCO : OH, 2.0),
(PU : MAM, 25 : 75); (- - - -) CO + IPDI + MAM (NCO : OH, 2.0), (PU : MAM, 35 : 65).

temperature range 300–400°C. Because the structure of the IPNs is very complicated, the process is bound to be slower in this region. But in the temperature range 410–500°C, the polyacrylamide and polymethacrylamide attached to the backbone of ricinoleic acid decomposes at a faster rate, and, hence, the energy of activation is low. These values correlate with the structural decomposition of the IPNs, as predicted by the mechanism. As the IPNs are very complicated in structure, it is very difficult to predict the exact decomposition pathway with the temperature increase. Further work to predict the actual method of decomposition is underway.

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