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Determination of the structural arrangements of ketene oligomers using NMR, FT-IR and ESI-MS

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Abstract

Oligomer of ketene was synthesized using glycine as the source material in presence of free electron rich carbon through free radical mechanism. The structure and the compositions were determined by using $^{13}C\{^{1}H\}$ NMR and DEPT – 135 spectroscopy measurements. Two-dimensional heteronuclear (HETCOR) NMR spectroscopy was used to resolve the ^{1}H NMR spectrum of the polymer. The NMR spectra reveal that the oligomers were generated as oligoester (OE), oligoketene (OK) and oligoacetal (OA) structural units. ESI-MS and ATR-FTIR also support these types of structural units in the crude polymer.

Keywords: Ketene oligomer; Free electron rich carbon; Glycine; NMR; ESI-MS

1. Introduction

Ketenes are derivatives of carboxylic acid, which contains the system of olefinic and carbonyl double bonds (C=C=O). In the absence of Ketenophiles, simple ketenes undergo self-addition to lead to oligomers and polymers [1]. Although ketenes are highly toxic in nature, when it gets polymerized yields a non-toxic and useful reactive chemicals. Ketene and its polymer constitute a class of compounds of great interest in organic synthesis as well as in polymer science. Environmental pollution by polymer materials is a global problem that needs to be addressed. But polymer and oligomer of ketenes attracted considerable interest from both academic and industry in recent years, as it is biodegradable [2–4]. Ketene polymers possess excellent properties like good tensile strength, good chemical and wear resistance, very low permeability and good impact behavior over a broad temperature range [5]. These properties give them significant commercial potential in a broad range of engineering, barrier packaging, fibre and blend applications.

Organic synthesis on insoluble supports remains until now only weakly developed [6–8]. The use of the insoluble support as a catalyst is an attractive approach since it allows simple isolation of the desired compound, easy elimination of by products and excess reagents, and facile separation and recovery of the material [9]. In this study, we used mesoporous carbon, which contains free electrons as the insoluble support.

Ketenes [10] and dimethyl ketenes [11,12] are generally taken as the monomers for the synthesis of ketene polymers, but for the first time we have tried using amino acids (a non-toxic source) as the starting material and we successfully achieved the synthesis of ketene oligomers through free radical mechanism. Amino acids can possess variety of intramolecular interactions, they are conformationally flexible molecules, they have many internal rotational degrees of freedom and repulsion of lone pair of electrons of N and O atoms which have a destabilization effect [13]. Hence the catalytic type of reactions involves molecular interactions and orientations, we chosen amino acid as the reactant for the synthesis of ketene oligomers through free electron rich carbon. Hence source material

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is rich in nitrogen and the end product ketene oligomer does not contain any nitrogen group the detail study in the structure of the end product is needed. In this paper, we reported the structure in detail of the oligomer obtained using glycine as the reactant.

The NMR spectroscopy studies have been used as the most reliable technique to determine compositional and stereo chemical structure of the polymers [14–17].

In this work, we report the complete ^{1}H and $^{13}C\{^{1}H\}$ NMR spectral assignments, ESI-mass spectrum and ATR-IR spectrum of the ketene oligomers. The compositions of the ketene oligomers as different structures were determined from $^{13}C\{^{1}H\}$ NMR spectra and the sequence distribution of the oligomer was done with the help of 2D NMR spectroscopy. The $^{13}C\{^{1}H\}$ NMR and ^{1}H NMR spectra of the oligomer are quite complex and has been assigned with the help of DEPT – 135 (distortionless enhancement by polarization transfer) and 2D heteronuclear (HETCOR) NMR spectroscopy. We have also confirmed the absence of nitrogen group in the product through elemental analysis, ^{14}N and ^{15}N NMR hence the reactant contains amino group (not reported).

2. Experimental

2.1. Preparation of ketene oligomers

Different weights of Glycine (E-merck, Germany) 25, 50, 75 and 100 mg were dissolved in 1 ml of water separately and made up to 250 ml with methanol. The above mixture was fed into the spiral packed bed reactor at the flow rate of 1.0 ml/min. The reactor was comprised of free electron rich carbon (insoluble catalyst) of different weights such as 6, 12, 18 and 24 g, which was maintained at the temperature of 10 °C (optimized). The solution collected at the outlet is subjected to conventional separation such as solar evaporation or vacuum distillation, whereby the alcohol escapes leaving behind the ketene oligomer. The ketene oligomer solution is optionally subjected to non-polar solvent extraction.

2.2. NMR measurements

The ^{1}H, $^{13}C\{^{1}H\}$ and DEPT NMR spectrum of the ketene oligomers was recorded in $CDCl_3$ on Bruker AMX-400 MHz spectrometer. The ^{1}H NMR measurements were carried out at the operating frequency of 400.134 MHz; spectral width, sw = 7246.381 Hz; acquisition time, at = 1.13 s; relaxation delay, $d_1 = 1.0$ s; $T = 300$ K and TMS as the internal standard. ^{13}C NMR spectrum was recorded at the operating frequency of 100.614 MHz; spectral width, sw = 25,000 Hz; acquisition time, at = 0.33 s; relaxation delay, $d_1 = 3.0$ s; $T = 300$ K and TMS as the internal standard. DEPT spectrum was recorded at the operating frequency of 100.614 MHz; spectral width, sw = 26315.789 Hz; acquisition time, at = 0.35 s; relaxation delay, $d_1 = 3.0$ s; $T = 300$ K and TMS as the internal standard.

The 2D-HETCOR NMR spectrum was recorded in $CDCl_3$ on JEOL ECA-500 MHz spectrometer. The 2D-HETCOR NMR measurements were carried out at the operating frequency of x is 125.765 MHz and the operating frequency of y is 500.159; x-acquisition time, $x$at = 0.14 s; y-acquisition time, $y$at = 0.13 s relaxation delay, $d_1 = 1.5$ s; $T = 293$ K.

2.3. ESI-MS measurements

The ESI (electron spray ionization) mass spectrum was recorded on Micromass QuattroII triple quadrupole mass spectrometer that was set in the positive ionization mode. The sample was dissolved in methanol and introduced into the ESI source through a syringe pump at the rate of 5 μl/min. The ESI capillary was set at 3.5 kV and the cone voltage was 40 V. The source temperature was 120 °C and the dessolvation temperature was 300 °C. The spectrum was collected in 6 s scans.

2.4. ATR-FTIR measurements

The ATR-FTIR spectrum was recorded on Thermo Nicolat – 320 spectrometer (AVATAR model) using the ATR attachment at room temperature. Sample was placed in a platinum liquid cell assembled in the ATR attachment. The spectrum was taken with a resolution of 4 cm^{-1} and accumulation of 32 scans. The fourier self-deconvoluted (FSD) IR spectrum was obtained with bandwidth of 15 and enhancement of 2.5 using EZ OMNIC 6.0 (Thermo Nicolat) software.

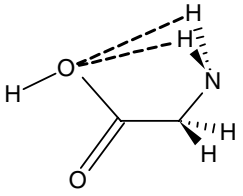
3. Results and discussion

3.1. Preparation of ketene oligomers

The formation of ketene from glycine is shown in the Eq. (1).

$$NH_2{-}CH_2{-}COOH \rightarrow CH_2{=}C{=}O + NH_2OH \quad (1)$$

The possible pathway of occurrence of the above products through catalytically is discussed below. Because of the hydrophilic nature of the free electron rich carbon, when the glycine molecule tries to enter into the pores of the catalyst it changes its orientation, due to the presence of the free electrons in the carbon (confirmed by the EPR studies) it forms an isomer having the two center-three electron interactions between NH_2 and OH groups as follows:

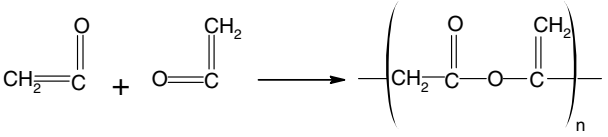


Glycine radical ions present a shorter –NH···O hydrogen bond (2.10 Å) [18]. As the intramolecular hydrogen bond interaction strengthens, the molecule undergoes over strain, which weakens the bond between C–N and C–OH. Thus the bond cleavage takes place between C–N and C–OH.

The explained mechanism is confirmed by the observation of hydroxylamine in the reaction, which was used as a tool for determining the conversion of ketene from amino acid. The hydroxylamine was estimated in the reaction mixture collected at the outlet of the spiral reactor by converting it into ferric hydroxamates using dimethylformamide and ferric chloride [19]. The yields and percentage conversion for the different loading rate and different weight of the catalyst are shown in the Table 1. The conversion percentage depends both on the monomer concentration and the catalyst concentration.

Ketenes are isoelectronic with isocyanates, we can place partial negative charge on both the end carbon and oxygen atoms and a partial positive charges on the central carbon atom [20]. The structure of the polymer depends upon the propagating anion in the polymerization reaction. The propagating anion may form either on the carbon or on the oxygen atom, generating either a carbanion or an enolate anion. Oligoketene are obtained by carbon–carbon addition. Acetal structures are formed by carbon–oxygen addition, while mixed addition gives the ester structure [21].

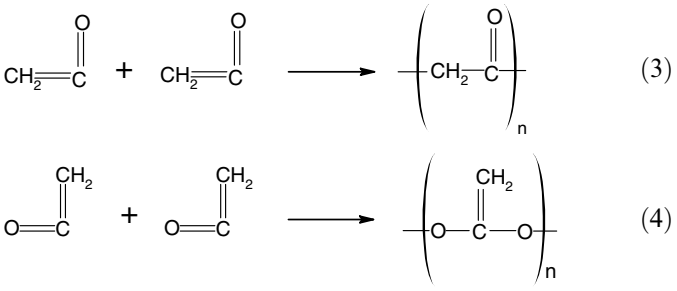
The carbon prepared has got both the Lewis acidic and basic sites. Therefore, ketene undergoes oligomerization to yield oligomer with ester, ketone and acetal structure as shown in the Eqs. (2)–(4).



(2)

Table 1
Correlation between the weights of the catalyst with the loading rate of the glycine as percentage conversion

S. No.	Weight of the catalyst (g)	Weight of glycine (mg)	Product yield (mg)	Conversion (%)
1	6	25	14.2	56.8
		50	23.6	47.2
		75	24.9	33.2
		100	21.7	21.7
2	12	25	18.3	73.2
		50	32.1	64.2
		75	36.5	48.7
		100	31.0	31.0
3	18	25	22.3	89.2
		50	38.4	76.8
		75	39.3	52.4
		100	43.9	43.9
4	24	25	22.4	89.6
		50	38.5	77.0
		75	39.1	52.1
		100	58.7	58.7

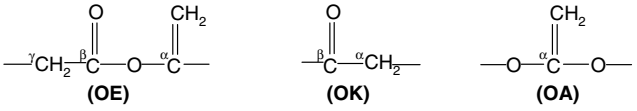


(3)
(4)

Therefore the conversion of ketene to ketene oligomers is also depends on the quantity of carbon used.

3.2. $^{13}C\{^1H\}$ NMR studies

The complete assignment of the $^{13}C\{^1H\}$ NMR spectrum of the ketene oligomer in $CDCl_3$ is shown in the Fig. 1. The generation of oligomers as oligoester (OE), oligoketene (OK) and oligoacetal (OA) structural units are represented as follows.



The α-methylene carbon resonances of OE are assigned around δ130.7 ppm. The peak around δ27.8 and δ58 ppm are due to γ-methylene resonances of OE and α-methylene resonances of OK, respectively. The quaternary carbon resonance of the OE and OA can be assigned without ambiguity with the help of DEPT-135 experiments. The signals at δ132 ppm can be assigned to the α-quaternary carbon of OE. In the DEPT – 135 experiment (Fig. 2) the signals present at negative phase shows the presence of methylene

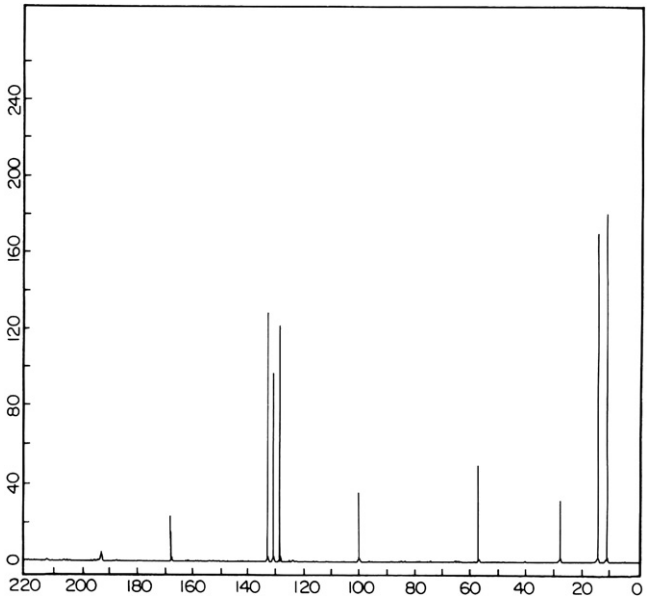


Fig. 1. The $^{13}C\{^1H\}$ spectrum of the ketene oligomers in $CDCl_3$.

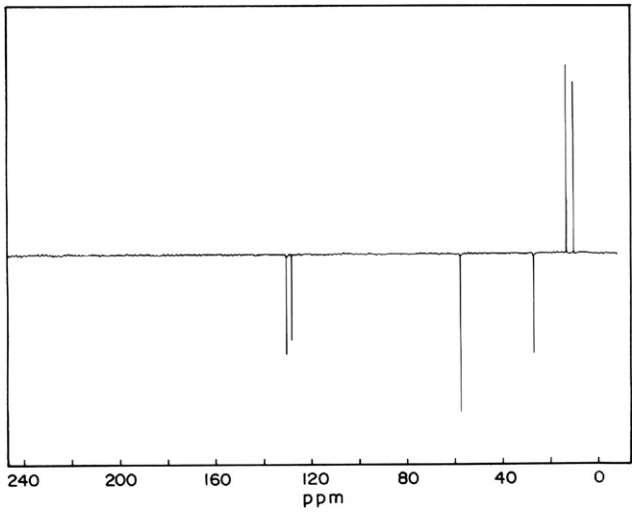


Fig. 2. The DEPT – 135 spectrum of the ketene oligomers in $CDCl_3$.

carbon signals apart from the quaternary carbon, the carbonyl carbon and ester carbon. The signals at δ193 and δ167 ppm can be assigned to the carbonyl carbon of OK and ester carbon group OE, respectively. The methylene carbon resonances of OA can be assigned at δ128 ppm. The signals around δ101 ppm are assigned to the quaternary carbon present in the OA.

The expanded $^{13}C\{^1H\}$ NMR spectrum of the ester carbonyl carbon resonances of OE is shown in the Fig. 3. The signals around δ167.8–167.6 ppm, δ167.6–167.3 ppm and δ167.2–167.0 ppm are assigned to mm, mr and rr triads with the help of the $^{13}C\{^1H\}$ NMR spectrum of OE structural arrangement of ketene oligomers. The triad tacticities were mm = 0.39, mr = 0.48 and rr = 0.13.

3.3. Two-dimensional HETCOR NMR studies

The 2D-HETCOR NMR spectrum of ketene oligomers recorded in $CDCl_3$ is shown in the Fig. 4 along with the complete signal assignments. The cross peaks at δ27.9/2.81 and δ58/3.73 ppm are assigned to γ-methylene group of OE and α-methylene group of OK, respectively, with

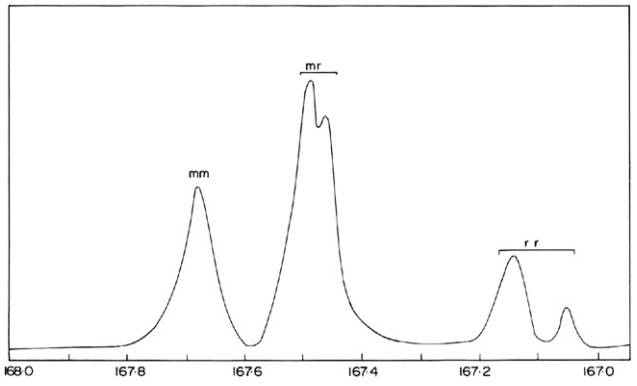


Fig. 3. The expanded $^{13}C\{^1H\}$ NMR spectrum of the ester carbonyl carbon resonances of OE.

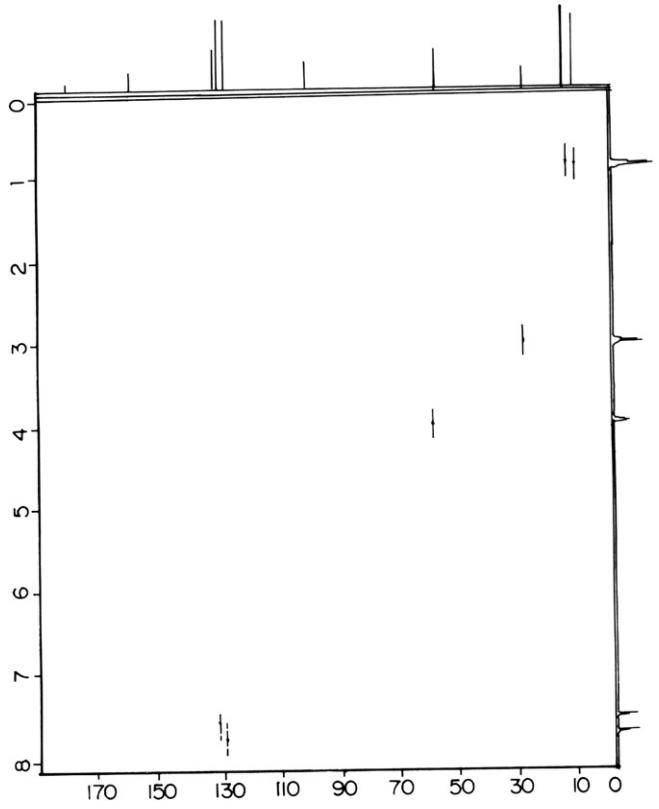


Fig. 4. Two-dimensional HETCOR spectrum of the ketene oligomers in $CDCl_3$.

the help of the $^{13}C\{^1H\}$ NMR spectrum. The expanded two-dimensional HETCOR NMR spectrum of α-methylene regions present in OE and OA is shown in Fig. 5. The cross peaks centered at δ130.84/7.46, δ130.84/7.54 and δ130.84/7.66 ppm are assigned to triad compositional sequences of α-methylene group of OE. The triad compositional sequences of α-methylene group of OA are centered at δ128.81/7.47, δ128.81/7.65 and δ128.81/7.83 ppm.

3.4. ^1H spectrum studies

The ^1H NMR spectrum along with the complete signal assignments is shown in the Fig. 6. The overlapped resonance signals in the ^1H NMR spectrum are assigned by one to one correlations between carbon and proton with the help of two-dimensional HETCOR NMR spectrum. The spectral region around δ0.6–1.0 ppm can be assigned to the methyl protons present at the end of the polymer chain and the α-methylene proton of OE and OA are present around δ7.4–7.8 ppm. The peak centered at δ2.81 and δ3.73 ppm can be assigned to the γ-methylene proton of OE and α-methylene proton of OK, respectively.

The unit ratio of the OE, OK and OA for the different conditions were calculated using the integration of the chemical shift of methylene group present in each unit and tabulated in Table 2. From the table it can be concluded that the formation of OE unit is maximum when

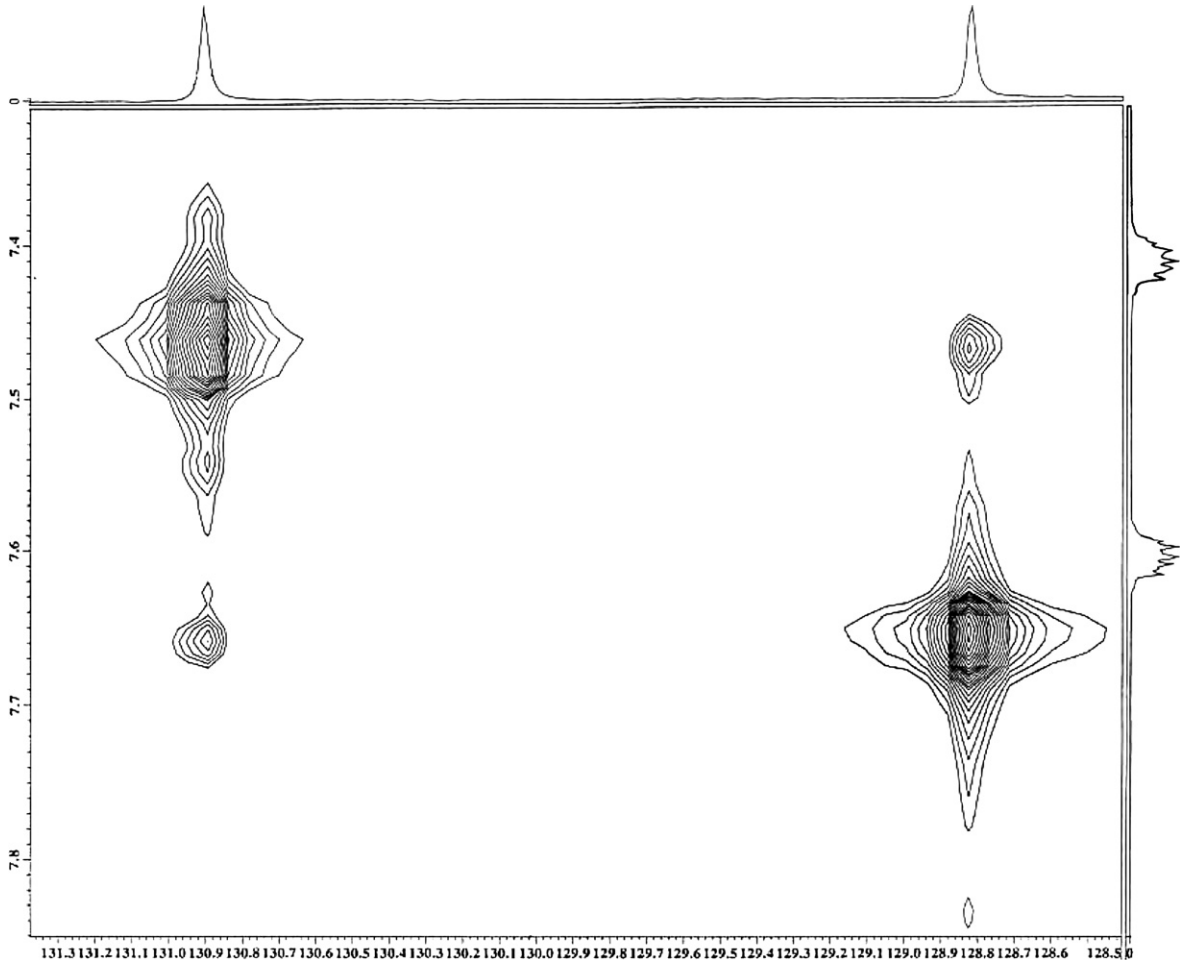


Fig. 5. The expanded α-methylene regions present in OE and OA in two-dimensional HETCOR spectrum.

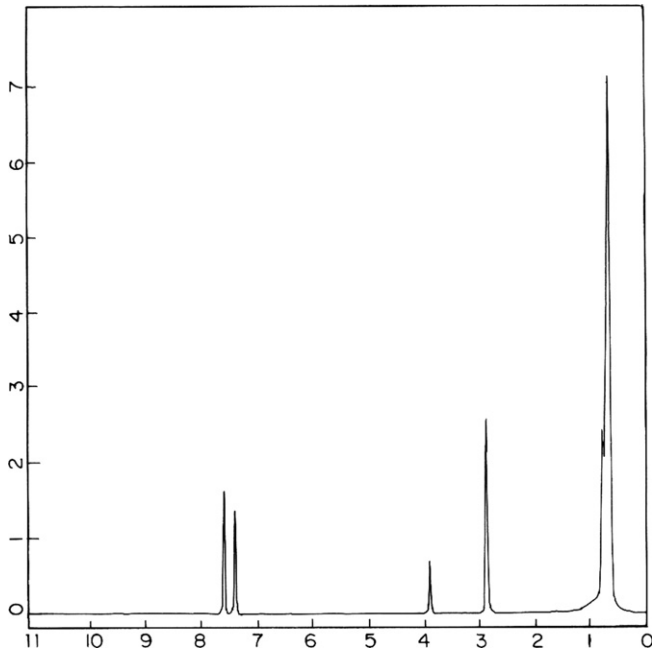


Fig. 6. The ^{1}H spectrum of the ketene oligomers in $CDCl_3$.

Table 2
Ratio of the different structural units of the oligomer determined using proton NMR

S. No.	Weight of the catalyst (g)	Weight of glycine (mg)	Unit ratio		
			OE	OK	OA
1	6	50	1	0.386	0.446
		75	1	0.357	0.444
2	12	50	1	0.392	0.427
		75	1	0.377	0.455
3	18	50	1	0.360	0.652
		75	1	0.371	0.658
4	24	50	1	0.506	0.716
		75	1	0.497	0.722

compared with the units of OK and OA apart from the catalyst and reactant concentration.

3.5. ESI-MS measurements

The product ion mass spectra of the oligomers are reported in Fig. 7. The positive electronspray ionization produced the protonated molecular ions $[M + H]^+$ at m/z

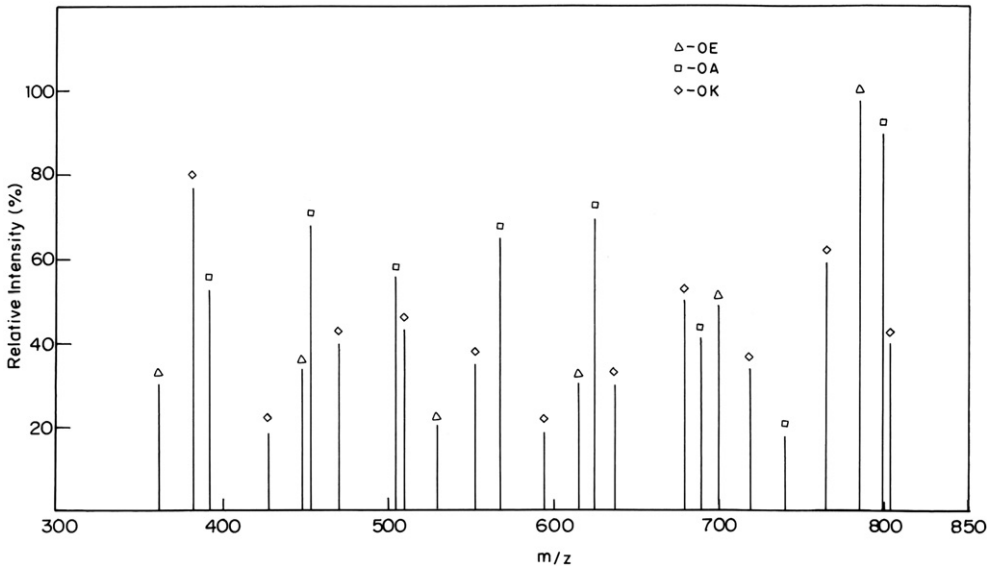


Fig. 7. ESI-MS mass spectrum of the ketene oligomers representing the different structural units (Δ, OE; □, OA; ◊, OK).

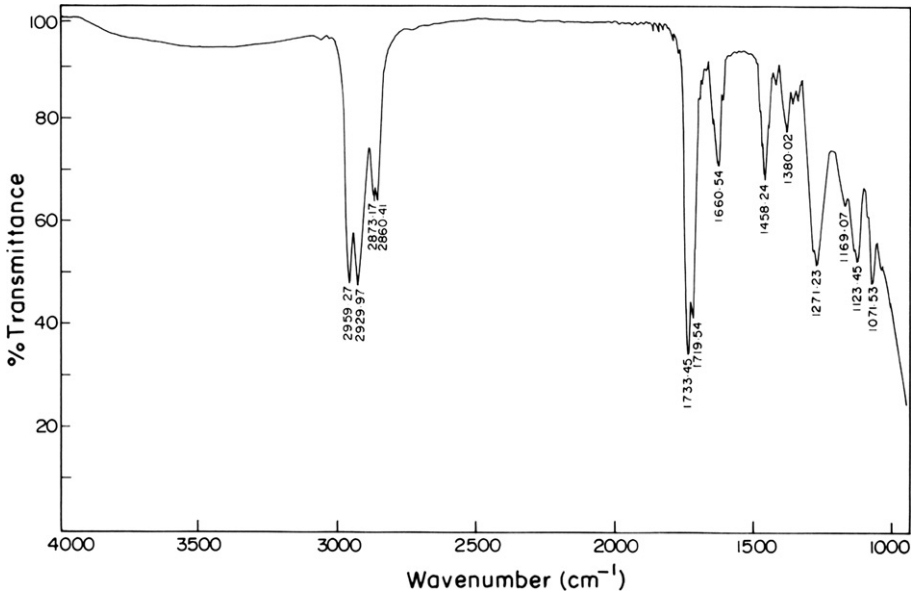


Fig. 8. FT-IR spectrum of the ketene oligomers.

804.7, 799.7 and 783.8 corresponds to the OK, OA and OE, respectively. The pattern observed clearly indicates the presence of the three series of fragment ion peaks that are separated by m/z 84 (denoted as Δ), m/z 58 (denoted as □) and m/z 42 (denoted as ◊), which is equivalent to the repeat unit mass of OE, OA and OK, respectively. The presence of signals of this type of structural arrangements confirm the presence of OE, OK and OA structural units as discussed in NMR measurements.

3.6. ATR-FTIR studies

The FT-IR spectrum of the ketene oligomers is shown in Fig. 8. The asymmetrical and symmetrical stretching of the methylene groups present as the backbone of the oligomer occurs near 2929.97 and 2860.41 cm^{-1}, respectively. The two distinct bands occurring at 2959.27 and 2873.17 cm^{-1} refers to the presence of end methyl groups. The band appears at 1458.24 cm^{-1} is due to the overlapping of asymmetrical bending vibration of methyl group with the scissoring vibration of methylene groups and the symmetrical bending vibration appears at 1380.02 cm^{-1}.

The C–C(=O)–C stretch due to OK structural unit is shown at the wavenumber of 1169.07 cm^{-1}. The C=O stretching of OK, the characteristic band of ketone group is appears at 1719.54 cm^{-1} as a shoulder with the C=O stretching of ester group in OE which is centered at 1733.45 cm^{-1}. The band centered at 1271.23 cm^{-1} can be

attributed to the C–O stretching vibration of the ester group in OE. The –C=CH_2 group present in OE and OA appears at 1660.54 cm^{-1}. The most characteristic absorption is the presence of strong band at 1123.45 cm^{-1} which can be attributed to the asymmetrical C–O–C stretching (OA). These IR spectral assignments also prove that the crude polymer is a mixture of three structural units of OE, OK and OA.

4. Conclusion

The $^{13}C\{^1H\}$ NMR, ^1H NMR and 2D NMR, ESI-MS and FTIR spectral assignments confirm that the formation of ketene oligomers from glycine through free radical mechanism using free electron rich mesoporous carbon as the catalyst. The HETCOR 2D NMR spectrum suggested the various structural arrangements (OE, OK and OA) of the polymeric chains due to the various functional groups of the carbon. The OA methylene carbon resonance structures are assigned to triad compositional sequences.

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