



Research Article

# Influence of ultrasound on multi-site phase transfer catalyzed polymerization of *N*-vinyl carbazole in two phase system

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## Abstract

Carbazole—containing motifs are of most desired materials because of its wide range of applications due to  $\pi$ -extended systems, molecular and optical properties was easily tunable via diverse structural modifications. Herein, we reported an efficient and facile polymerization of *N*-vinyl carbazole (NVK) using multi-site phase transfer catalyst with and without ultrasound condition. The rate of polymerization ( $R_p$ ) was effectively improved with ultrasound in short time on compare with silent condition. Role of different parameters such as variation of frequency, monomer, initiator, catalyst and temperature, solvents, aqueous and pH on the rate of polymerization of NVK was explored under silent and ultrasound condition (45 kHz/550 W). Activation energy of polymerization was supported for an enhancement of rate under ultrasound condition. From the experimental results, an appropriate kinetic model and role of various parameters in polymerization reaction was discussed. The obtained poly (*N*-vinyl carbazole) was confirmed and characterized by FT-IR, <sup>1</sup>H NMR, TGA and XRD techniques.

**Keywords** Ultrasound · Multi-site phase transfer catalyst · Kinetics of polymerization · Rate of polymerization · *N*-vinyl carbazole

## 1 Introduction

Carbazoles are classical class of nitrogen-based heterocyclic, possessing of two benzene rings in central pyrrole motif. Carbazole based polymeric materials have attracted much interest in scientific and industrial arena [1–3] and it was considered one of the best desired materials for versatile applications [4, 5] due to facile  $\pi$ —extended systems, easily tunable structures and their natural features of hole-transporting, high charge-carrier mobility and electroluminescent properties [1, 6]. The capability of hole-transporting properties of carbazole was useful in organic electronics applications [7]. Among various carbazole based polymers, a great attention was placed for poly (*N*-vinyl carbazole) (PNVK) because of easy synthesis

and good solubility in common organic solvents [8]. PNVK was a class of promising photoconductive materials used in photocopiers, laser printers, printing plates, and electro-photographic microfilming [9].

Polymerization of *N*-vinyl carbazole (NVK) was investigated extensively using different methods, for instance, free radical [10], cationic polymerization [11], anionic polymerization [12], nitroxide-mediated polymerization (NMP) [13–15], atom transfer radical polymerization (ATRP) [16–20], reversible addition-fragmentation chain transfer (RAFT) polymerization [21–26], charge transfer [27], electrochemical [28] and solid state polymerization [29, 30], single electron transfer-living radical polymerization (SET-LRP) [31], organo-hetero atom mediated living radical polymerization [32], and organometallic-mediated radical

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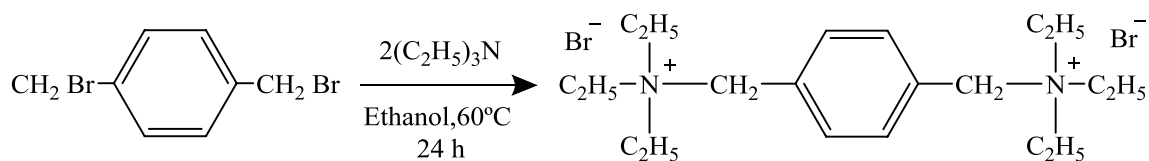
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polymerization [33] etc. Ultrasound condition was used in various organic and polymerization reactions to improve the rate of reaction, facilitates the reactions at ambient conditions etc. [34–40]. In recent years, ultrasound coupled with phase transfer catalyzed radical polymerization of *N*-vinyl imidazole [41] and different alkyl methacrylates such as methyl methacrylate [42], ethyl methacrylate [43], glycidyl methacrylate [44] were reported. Consequently, we have also reported ultrasound aided single-site phase transfer catalyzed polymerization of methyl methacrylate [45] and acrylonitrile [46]. In spite of the various methods are reported for the polymerization of *N*-vinyl carbazole, to the best of our knowledge, the polymerization of *N*-vinyl carbazole by multi-site phase transfer catalyst and ultrasound conditions has not yet reported. This motivated us to work on polymerization of *N*-vinyl carbazole (NVK) using 1,4-*bis* (triethyl methyl ammonium) benzene dibromide (TEMABDB) as multi-site phase transfer catalyst (MPTC) and potassium peroxydisulphate (PDS) as water soluble initiator at  $40 \pm 2$  °C in two phase system under unstirred nitrogen atmosphere with silent and ultrasound condition (45 kHz/550 W). Ultrasound condition facilitate the polymerization process effectively with two-fold enhancement of yield at short-duration on compare with silent condition. Influence of various experimental parameters on the rate of polymerization was ascertained in both conditions and suitable mechanism was proposed.

## 2 Experimental

### 2.1 Materials and solvents

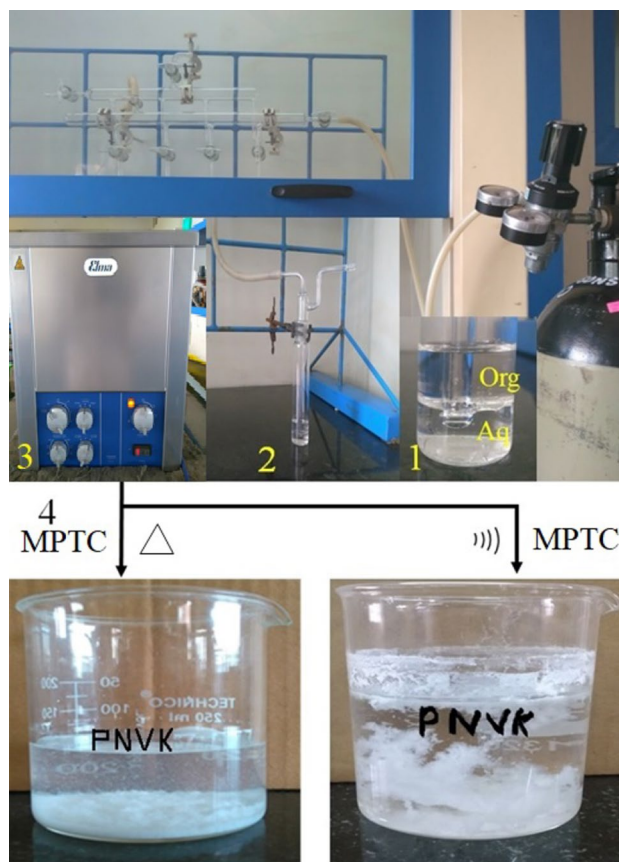
The starting materials 9-Vinylcarbazole (98% of pure, NVK) and initiator, potassium peroxydisulphate (99% of pure, PDS) was purchased from Sigma Aldrich, India used without further purification. The multi-site phase transfer catalyst, 1, 4-*bis* (triethyl methyl ammonium) benzene dibromide (TEMABDB) was synthesized by adopting the reported procedure as shown in the Scheme 1 [47]. The other solvents are extra-pure grade was used as received from Sigma-Aldrich, Avra and Finar, India. The ultra-pure water was used to make an aqueous phase.



**Scheme 1** Synthesis of multi-site PTC: 1, 4-*bis* (triethylmethylammonium) benzene dibromide (TEMABDB)

### 2.2 Instruments

The ultrasound generator having a thermostatic bath equipped with dual frequency (25 and 45 kHz and power of 550 W; Elma Ultrasonicator with dual frequency, Germany) was used for the polymerization (Shown in Fig. 1). <sup>1</sup>HNMR spectra of poly (*N*-vinylcarbazole) were recorded with BRUCKER 400 MHz spectrometer using CDCl<sub>3</sub> as solvent and tetramethylsilane (TMS) as an internal reference. FT-IR spectrum of polymer was recorded in (JASCO) the



**Fig. 1** Polymerization process setup: 1. Polymerization reaction tube consists of equal volume of aqueous and organic phase 2. De-aeration of reaction mixture. 3. Dual frequency Ultrasonicator equipped with thermostatic bath (25 and 45 kHz). 4. Differences in the rate of precipitations of PNVK under ultrasound (right) and silent (left) condition

spectral range from 4000 to 400  $\text{cm}^{-1}$ . The thermal analysis of poly (*N*-vinylcarbazole) was carried out by using Inkar Instrument. The sample weight 3.012 mg was loaded in alumina pans and ramped at heating rate 20  $^{\circ}\text{C}$  per minutes from ambient to 700  $^{\circ}\text{C}$  in nitrogen atmosphere. The powder XRD pattern of the polymer was analyzed using Rigaku X-ray diffractometer.

### 2.3 Polymerization of *N*-vinyl carbazole (NVK)

The polymerization reactions were carried out in Pyrex glass tubes provided with inlets and outlets for nitrogen. The monomer (NVK) was dissolved in cyclohexane was the organic phase. The catalyst, ionic and acid strength of phase was adjusted by adding known reagents in the aqueous phase. An equal volume of reaction mixture was thoroughly de-aerated for 20 min. The ultrasound equipment was set in a constant temperature ( $40 \pm 1$   $^{\circ}\text{C}$ ) with ultrasound condition of 45 kHz; 550 W. The known concentration of initiator was added to reaction tube, which was placed in ultrasonicator, polymerization was started and poly (*N*-vinylcarbazole) (PNVK) precipitated continuously during polymerization (Scheme 2). After a stipulated time period, the reactions were stopped by pouring the reaction mixture into ice-cold methanol. The polymer was re-precipitated using high pure water and it was filtered through a sintered glass crucible with repeated washing with pure water then dried using vacuum pump after that kept in desiccators to get a constant weight at room temperature. The kinetics of polymerization was examined by tuning the various parameters such as frequency, monomer, initiator, catalyst, solvents, pH and temperature by adopting the aforementioned procedure (Fig. 1). The rate of polymerization ( $R_p$ ) was determined gravimetrically from the weight of the polymer formed.  $R_p$  was calculated from the weight of polymer obtained [45, 48]. The average yield of the polymer was lies between 70 and 75% for each variation of study.

### 2.4 Mechanistic path ways of polymerization

In two phase reactions, the rate of reaction was attributed to interaction and diffusion between phases. The reaction between immiscible phases was dead slow because of

poor collision and diffusion. An easy way to solve such difficulty is to perform the reaction at high temperature and using a co-solvent. However, such conditions are also creates side reactions and complexity in choosing co-solvent. Generally, this kind of situation in two phase system, the rate of reaction is effectively improved by the use of phase transfer catalyst (PTC). PTC capable of extract and transfer ionic reactants of aqueous and or solid phase into organic phase, where the reaction will take place.

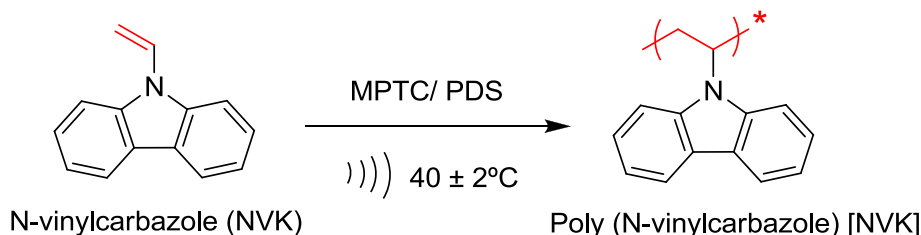
On the basis of experimental observations, the mechanistic path ways of polymerization of *N*-vinyl carbazole in the presence of multi-site phase transfer catalyst under ultrasound condition was proposed. A simple ion exchange reaction between QX (quaternary ammonium salts, multi-site phase transfer catalyst) and KY (Initiator) was occurring to produce QY (quaternary ammonium peroxydisulphate complex) in the aqueous phase. The formed intermediate QY decomposes at the interface in the presence of heat and or ultrasound condition to yield radical anion. Thus generated radical anion was reacting with monomer (M) to form primary monomer radical and polymerization goes up by the successive addition of monomers as shown in Scheme 3 [46]. We observed that the polymerization reactions did not occur in presence of ultrasound alone and also absence of PTC, which proves the role of catalyst in the polymerization.

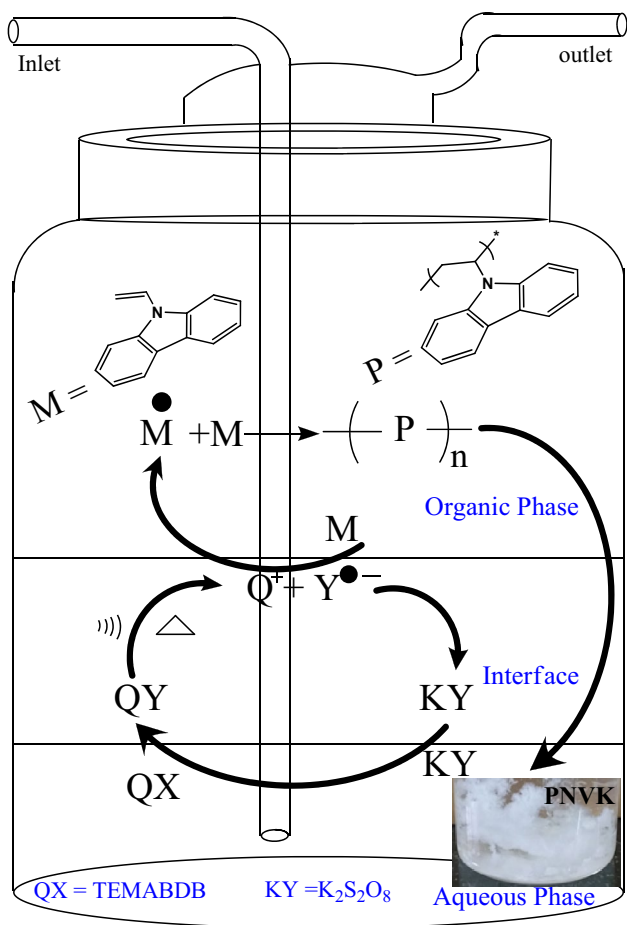
Role of Catalyst: The polymerization reaction was performed in the absence of catalyst under ultrasound and silent condition  $\sim 30$  min. The effective mixing/movement of two phase was take place with slight changes (turbid), then the reaction mixture was poured into methanol it was disappeared. This observation could be a confirmation of role of catalyst in the polymerization reaction.

## 3 Results and discussion

*N*-vinyl carbazole was polymerized in heterogeneous media by multi-site phase transfer catalyst using conventional water soluble initiator. The polymerization of NVK was carried out at  $40 \pm 2$   $^{\circ}\text{C}$  under the silent and ultrasound condition (45 kHz/550 W). To validate the polymerization kinetics, role of different factors such as frequency, monomer, initiator, catalyst and temperature, solvents, aqueous

**Scheme 2** Polymerization of NVK by multi-site phase transfer catalyst with ultrasound condition





**Scheme 3** Polymerization of NVK using multi-site PTC with ultrasound condition in two phase system

and pH variation on the rate of polymerization of *N*-vinyl carbazole was explored and its significance was discussed.

### 3.1 Rely of ultrasound power on polymerization

At the beginning, we have examined the dependence of ultrasound condition on the rate of polymerization of NVK-TEMABDB-PDS system with different ultrasound frequency of 0, 25 and 45 kHz with giving constant power of 550 W and results are presented in Table 1. The rate of polymerization ( $R_p$ ) was progressively increases with frequency. The high conversion was obtained at the 45 kHz/550 W

**Table 1** Rely of ultrasound condition on  $R_p$

0 kHz, $R_p \times 10^3 \text{ mol L}^{-1} \text{ min}^{-1}$	25 kHz, $R_p \times 10^3 \text{ mol L}^{-1} \text{ min}^{-1}$	45 kHz, $R_p \times 10^3 \text{ mol L}^{-1} \text{ min}^{-1}$
0.3040	0.4412	0.7158

Parameters condition: [NVK]:  $0.1 \text{ mol L}^{-1}$ ; [PDS]:  $4.0 \times 10^{-2} \text{ mol L}^{-1}$ ; [TEMABDB]:  $2.0 \times 10^{-2} \text{ mol L}^{-1}$ ;  $[\text{H}^+]$ :  $0.20 \text{ mol L}^{-1}$ ;  $[\mu]$ :  $0.50 \text{ mol L}^{-1}$ ; Temperature:  $40 \pm 2 \text{ }^\circ\text{C}$ ; Time :60 min

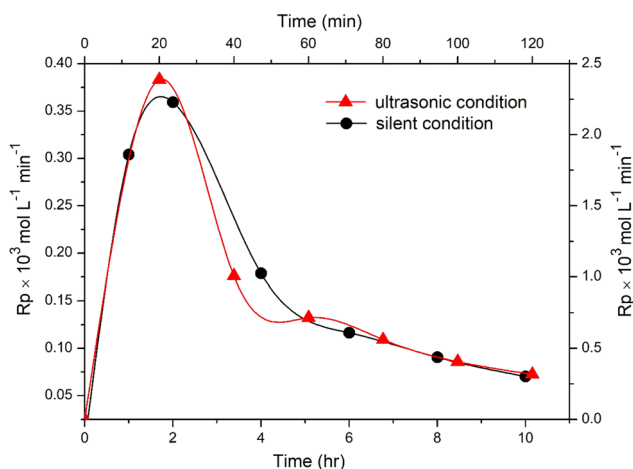
and it was fixed to evaluate various experimental parameters. Phase transfer catalyzed polymerization rate was doubled with use of ultrasound condition [42–46] and the enhancement of rate in the polymerization is due to chemical and physical effects of ultrasound [49].

### 3.2 Rely of time on the rate of polymerization ( $R_p$ )

The dependence of time on the rate of polymerization of *N*-vinylcarbazole was examined at different intervals of time by keeping other parameters are constant. The plot of  $R_p$  versus time showed the established trends as reported in various phase transfer catalyzed polymerization reactions [47, 48, 50]. The steady state rate of polymerization of NVK was arrived at 2 h and 60 min for silent and ultrasound condition respectively. Further, it was observed the rate of polymerization increases with short duration of reaction time in the presence of ultrasound on compare with silent condition (Fig. 2). This may be due to the effect of ultrasound which could improve the mixing of two phase effectively and making like homogenous phase or improve the formation of radicals [41–46].

### 3.3 Rely of [NVK] on the rate of polymerization ( $R_p$ )

The effect of *N*-vinylcarbazole concentration on the rate of polymerization ( $R_p$ ) was studied in the range from 0.10 to 0.35 mol/L at fixed other variables under ultrasound and silent condition. It was found that an increasing the concentration of monomer the rate increases for both conditions. Such a routine trends was reported for the phase transfer catalyzed polymerization of different alkyl methacrylates. However, the rate was doubled under ultrasound



**Fig. 2** Rely of time on rate of polymerization. Parameters condition: [NVK]:  $0.1 \text{ mol L}^{-1}$ ; [PDS]:  $4.0 \times 10^{-2} \text{ mol L}^{-1}$ ; [TEMABDB]:  $2.0 \times 10^{-2} \text{ mol L}^{-1}$ ;  $[\text{H}^+]$ :  $0.20 \text{ mol L}^{-1}$ ;  $[\mu]$ :  $0.50 \text{ mol L}^{-1}$ ; Temperature:  $40 \pm 2 \text{ }^\circ\text{C}$  Ultrasound condition: 45 kHz/550 W

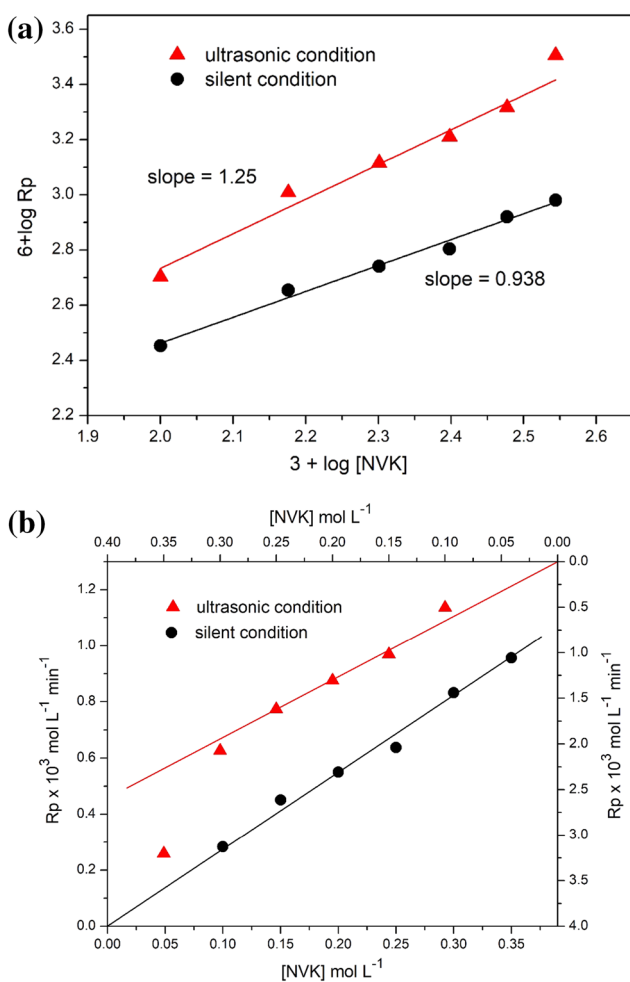


with short reaction time on compare with silent condition. A plot of  $6 + \log R_p$  versus  $3 + \log [NVK]$  with the slope was found to be 1.25 and 0.938 for ultrasound and silent condition respectively. The order of unity with respect to NVK was confirmed from the straight line passing through origin in the plot of  $R_p$  versus  $[NVK]$  (Fig. 3a, b). The order of unity with respect to monomer concentration was well documented in the polymerization of different vinyl monomers using multi-site PTC [45, 46, 51, 52].

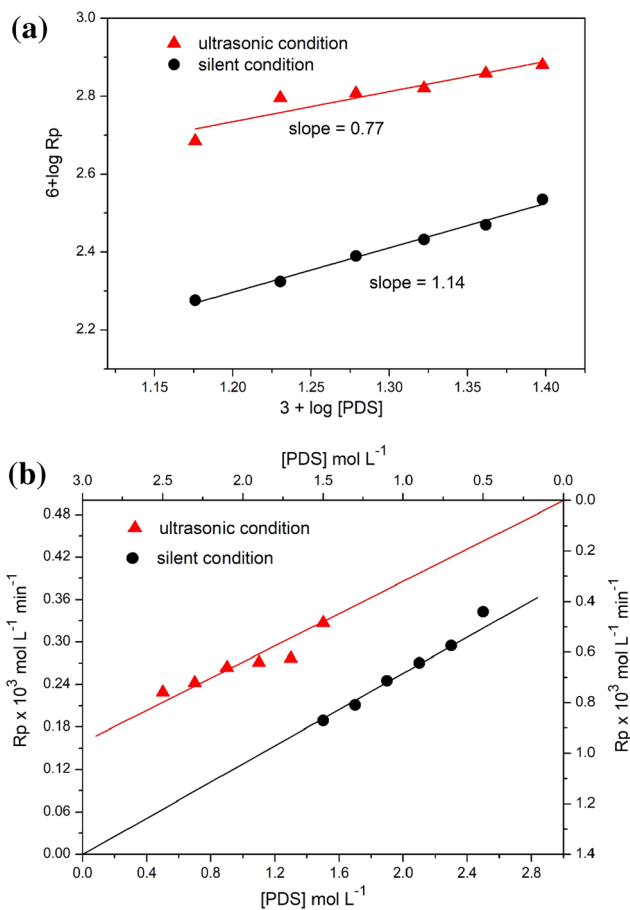
### 3.4 Rely of [PDS] on the rate of polymerization ( $R_p$ )

The effect of initiator concentrations in the range of 1.5–2.5 mol/L was explored on the rate of polymerization at fixed all parameters with ultrasound and silent condition. The  $R_p$  was doubled with ultrasound condition on compare with silent method. It could be explained by the

different radical formation mechanisms. In conventional radical polymerization, radicals are generated by thermal decomposition of initiator where as an ultrasound condition the formation of radicals are effectively improved by various routes like initiator dissociation or water molecule scission, direct exciting monomer or polymer chain etc. [42–44]. The reaction order with respect to initiator concentrations of silent and ultrasound condition was obtained from plot of  $6 + \log R_p$  versus  $3 + \log [PDS]$  was found to be 0.77 and 1.14 for both systems. The plot of  $R_p$  versus  $[PDS]$  was linear passing through the origin supporting the above deduction (Fig. 4a, b). The higher initiator order can be explained by gel effect or diffusion controlled termination constant [50]. In addition, higher order of initiator concentration suggests that the termination is bimolecular and monomer induced decomposition of PDS was absent. The greater than half order with respect to initiator concentration was reported in phase transfer catalyzed polymerization process [48, 51].



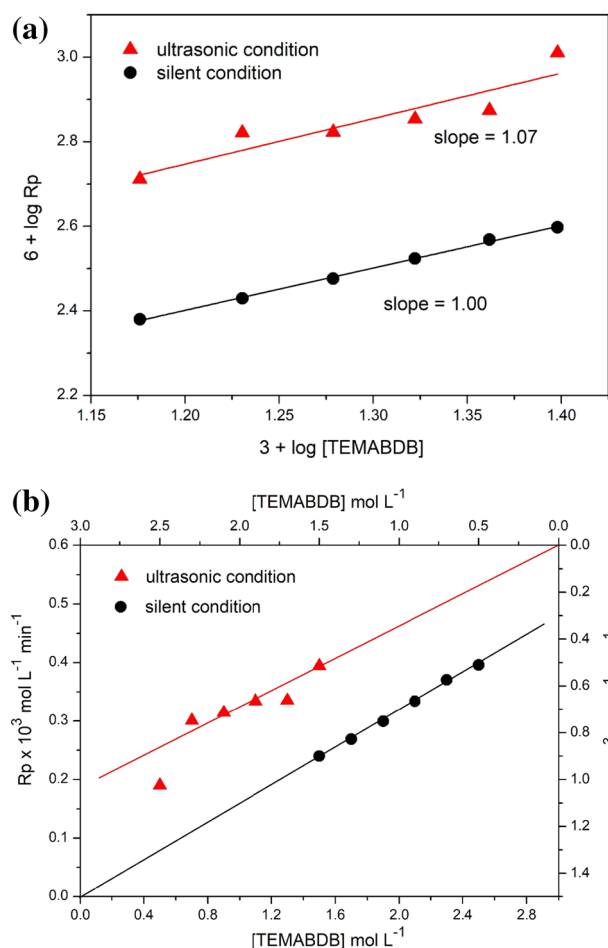
**Fig. 3** Rely of  $[NVK]$  on the  $R_p$ . **a** Plot of  $6 + \log R_p$  versus  $3 + \log [NVK]$ . **b** Plot of  $R_p$  versus  $[NVK]$ . Parameters condition:  $[PDS]$ :  $4.0 \times 10^{-2} \text{ mol L}^{-1}$ ;  $[TEMABDB]$ :  $2.0 \times 10^{-2} \text{ mol L}^{-1}$ ;  $[H^+]$ :  $0.20 \text{ mol L}^{-1}$ ;  $[\mu]$ :  $0.50 \text{ mol L}^{-1}$ ; Temperature:  $40 \pm 2 \text{ }^\circ\text{C}$ ; Ultrasound condition:  $45 \text{ kHz}/550 \text{ W}$



**Fig. 4** Rely of  $[PDS]$  on the  $R_p$ . **a** Plot of  $6 + \log R_p$  versus  $3 + \log [PDS]$ . **b** Plot of  $R_p$  versus  $[PDS]$ . Parameters condition:  $[NVK]$ :  $0.1 \text{ mol L}^{-1}$ ;  $[TEMABDB]$ :  $2.0 \times 10^{-2} \text{ mol L}^{-1}$ ;  $[H^+]$ :  $0.20 \text{ mol L}^{-1}$ ;  $[\mu]$ :  $0.50 \text{ mol L}^{-1}$ ; Temperature:  $40 \pm 2 \text{ }^\circ\text{C}$ ; Ultrasound condition:  $45 \text{ kHz}/550 \text{ W}$

### 3.5 Rely of [TEMABDB] on the rate of polymerization (Rp)

The role of multi-site phase transfer catalyst (TEMABDB) was varied from 1.5 to 2.5 mol/L to examine its effect on the polymerization rate at fixed other parameters for both conditions. From the observations, it was clear that as rate increases with rise of concentrations and two-fold excess of yield was obtained with ultrasound condition. It may due to presence of ultrasound was promote the mixing of phase, formation of more radicals and make ease the transport of ions between the phases. The slope of linear plot was obtained by plotting of  $6 + \log R_p$  versus  $3 + \log [\text{TEMABDB}]$ , the order with respect to [TEMABDB] was found to be 1.07 and 1.00 for ultrasound and silent condition (Fig. 5a, b). The observed order was confirmed from the straight line passing through the origin in a plot of  $R_p$  versus [TEMABDB]. The polymerization did

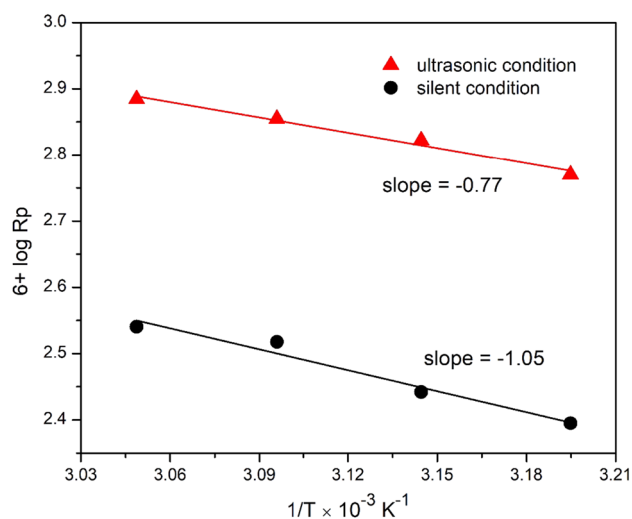


**Fig. 5** Rely of [TEMABDB] on the Rp. **a** Plot of  $6 + \log R_p$  versus  $3 + \log [\text{TEMABDB}]$ . **b** Plot of  $R_p$  versus [TEMABDB]. Parameters condition: [NVK]: 0.1 mol L<sup>-1</sup>; [PDS]:  $4.0 \times 10^{-2}$  mol L<sup>-1</sup>; [H<sup>+</sup>]: 0.20 mol L<sup>-1</sup>; [μ]: 0.50 mol L<sup>-1</sup>; Temperature:  $40 \pm 2$  °C; Ultrasound condition: 45 kHz/550 W

not occur in the absence of catalyst as well presence of ultrasound condition even after several minutes [43–46].

### 3.6 Rely of temperature on the rate of polymerization (Rp)

The effect of temperature on the polymerization of *N*-vinyl carbazole was investigated by varying the temperature of medium in the range of 40 °C to 55 °C. It was observed the rate of polymerization increase with raise in temperature because of formation more reactive radicals with high temperature as well ultrasound condition. The activation energy ( $E_a$ ) was obtained from the Arrhenius plot of  $6 + \log R_p$  versus  $1/T$  (Fig. 6). The activation energy ( $E_a$ ) of 14.78 kJ/mol and 20.10 kJ/mol was obtained for ultrasound and silent condition (Table 2). The activation energy of 36.41 kJ/mol was reported for the polymerization of *N*-vinyl carbazole using Co(II)-I3X molecular sieves [53]. Activation energy value ( $E_a$ ) of ultrasound condition was a vital evidences to supports the enhancement of rate with short duration on compare with silent condition.



**Fig. 6** Rely of temperature on the Rp. Parameters condition: [NVK]: 0.1 mol L<sup>-1</sup>; [PDS]:  $4.0 \times 10^{-2}$  mol L<sup>-1</sup>; [TEMABDB]:  $2.0 \times 10^{-2}$  mol L<sup>-1</sup>; [H<sup>+</sup>]: 0.20 mol L<sup>-1</sup>; [μ]: 0.50 mol L<sup>-1</sup>; Ultrasound condition: 45 kHz/550 W

**Table 2** Thermodynamic parameters

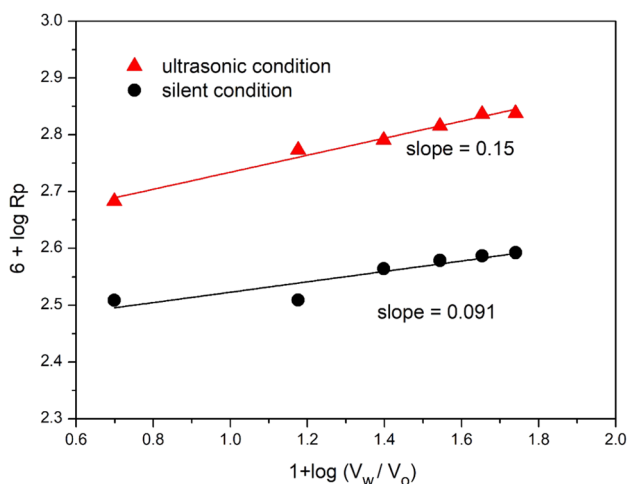
Condition	$E_a$ , kJ/mol	$\Delta G^\ddagger$ , kJ/mol	$\Delta H^\ddagger$ , kJ/mol	$\Delta S^\ddagger$ kJ/mol
Ultrasound	14.78	34.16	12.12	-109.15
Silent	20.16	40.28	12.36	-134.43

### 3.7 Rely of aqueous phase on the rate of polymerization (Rp)

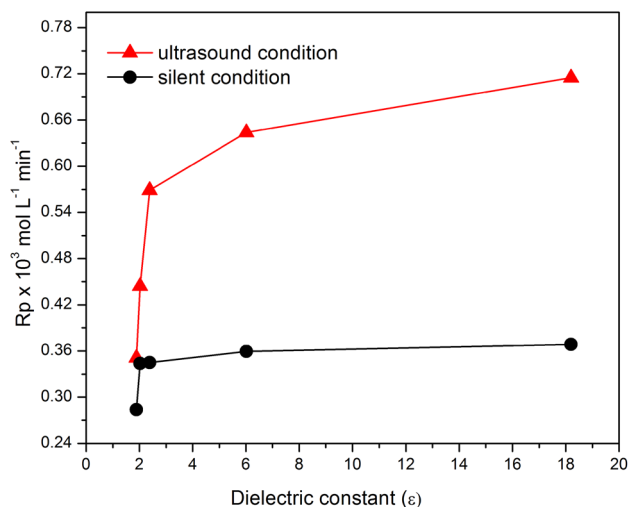
Polymerization reactions was conducted with a constant volume of organic phase and varied volumes of aqueous phase ( $V_w/V_o = 0.5-5.5$ ) at fixed concentrations of all other parameters for both conditions. The variation of aqueous phase was found to exert no significant change in the rate of polymerization (Fig. 7). A similar kind of trends was observed in most of the phase transfer catalyzed radical polymerization using different alkyl methacrylates [45, 48, 50–52, 54].

### 3.8 Rely of water immiscible solvents on the rate of polymerization (Rp)

The effect of varying dielectric constant of the medium on the polymerization rate was explored using different solvents. The influence of various water immiscible solvents (cyclohexanone, ethyl acetate, toluene, cyclohexane and n-hexane) of dielectric constants and obtained Rp value were presented in Fig. 8 for both conditions. A two-fold enhancement in the rate was observed compare with silent condition. The reason for the observed increase may be due to the formation of greater number of initiating free radicals under ultrasound condition and also polarity of the solvents, which facilitates greater transfer of peroxydisulfate ion from aqueous phase to organic phase [45–48, 50].



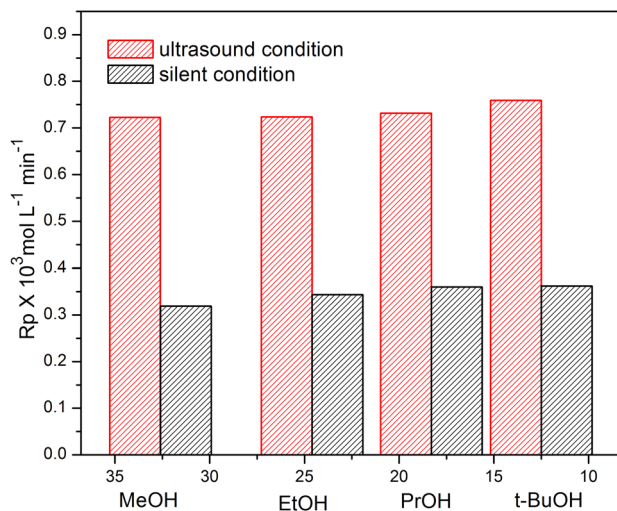
**Fig. 7** Rely of aqueous phase on Rp. Plot of  $6 + \log R_p$  versus  $[V_w]$ . Parameters condition: [NVK]:  $0.1 \text{ mol L}^{-1}$ ; [PDS]:  $4.0 \times 10^{-2} \text{ mol L}^{-1}$ ; [TEMABDB]:  $2.0 \times 10^{-2} \text{ mol L}^{-1}$ ;  $[H^+]$ :  $0.20 \text{ mol L}^{-1}$ ;  $[\mu]$ :  $0.50 \text{ mol L}^{-1}$ ; Temperature:  $40 \pm 2 \text{ }^\circ\text{C}$ ; Ultrasound condition: 45 kHz/550 W



**Fig. 8** Rely of water immiscible solvents on Rp. Plot of Rp versus Dielectric constants of solvents. Parameters condition: [NVK]:  $0.1 \text{ mol L}^{-1}$ ; [PDS]:  $4.0 \times 10^{-2} \text{ mol L}^{-1}$ ; [TEMABDB]:  $2.0 \times 10^{-2} \text{ mol L}^{-1}$ ;  $[H^+]$ :  $0.20 \text{ mol L}^{-1}$ ;  $[\mu]$ :  $0.50 \text{ mol L}^{-1}$ ; Temperature:  $40 \pm 2 \text{ }^\circ\text{C}$ ; Ultrasound condition: 45 kHz/550 W

### 3.9 Rely of water miscible solvents on the rate of polymerization (Rp)

An influence of various water miscible alcohols on the rate of polymerization was examined for both conditions at fixed concentrations of other parameters. The addition of water miscible alcohols in the polymerization medium has resulted moderate increase in the rate as shown in Fig. 9. The reason may attribute to formation of alkoxy radicals



**Fig. 9** Rely of water miscible solvents on Rp. Plot of Rp versus water miscible solvents. Parameters condition: [NVK]:  $0.1 \text{ mol L}^{-1}$ ; [PDS]:  $4.0 \times 10^{-2} \text{ mol L}^{-1}$ ; [TEMABDB]:  $2.0 \times 10^{-2} \text{ mol L}^{-1}$ ;  $[H^+]$ :  $0.20 \text{ mol L}^{-1}$ ;  $[\mu]$ :  $0.50 \text{ mol L}^{-1}$ ; Temperature:  $40 \pm 2 \text{ }^\circ\text{C}$ ; Ultrasound condition: 45 kHz/550 W

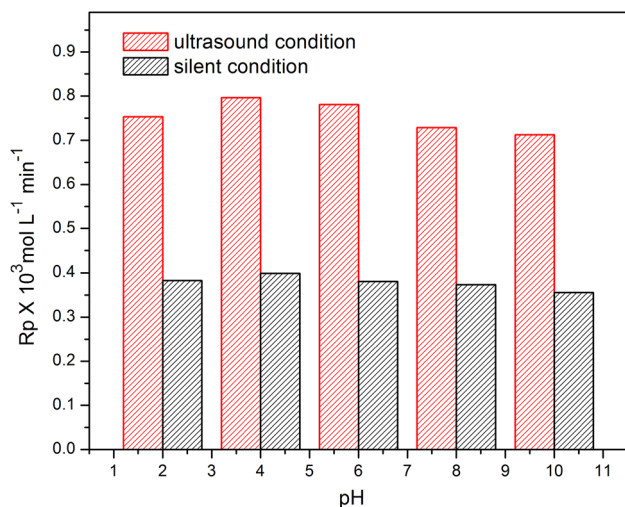
from added alcohols, which can further initiate the polymerization by formation of free radicals. This process could be accelerated under ultrasound condition.

### 3.10 Rely of pH on the rate of polymerization (Rp)

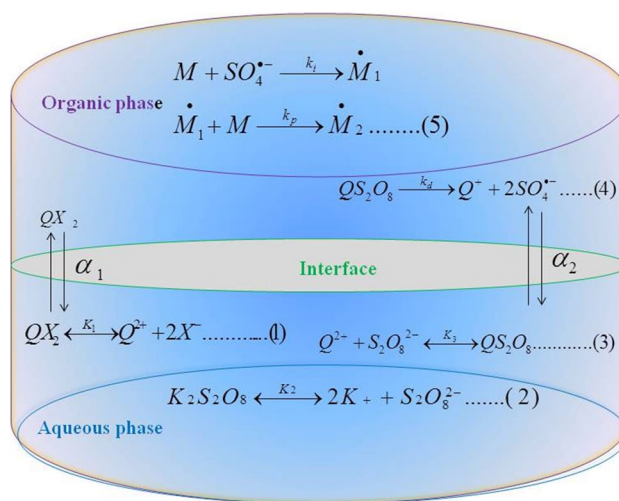
The role of pH is an important parameter in the polymerization reaction. The pH may influence the polymerization rate by coagulating the dispersed phase and affecting the initiation step. We have conducted the polymerization reaction at the pH range of 2 to 10 under both conditions (Fig. 10). Initially, an increase in the rate of polymerization thereafter gradual decrease was observed with the pH range of 2–10. This is due to peroxydisulphate initiated polymerization is negatively affected by the gradual addition of pH in the reaction medium. In the present study the polymerization reaction was conducted at pH of 2.0. This behaviour was reported in phase transfer catalyzed polymerization of vinyl monomers [45, 46].

### 3.11 Mechanism of phase transfer catalyzed radical polymerization of N-vinyl carbazole

Based on the observed experimental results, it was clear that effective polymerization process was accomplished in two phase system with help of multi-site phase transfer catalyst. However, the rate of polymerization was doubled with short duration under ultrasound condition. The mechanistic path ways of multi-site phase transfer catalyzed polymerization of N-vinyl carbazole using water soluble initiator was shown in Scheme 4. At the beginning, formation of  $QS_2O_8$  was take place in the aqueous phase



**Fig. 10** Rely of pH on Rp. Parameters condition: [NVK]: 0.1 mol L<sup>-1</sup>; [PDS]: 4.0 × 10<sup>-2</sup> mol L<sup>-1</sup>; [TEMABDB]: 2.0 × 10<sup>-2</sup> mol L<sup>-1</sup>; [μ]: 0.50 mol L<sup>-1</sup>; Temperature: 40 ± 2 °C; Ultrasound condition: 45 kHz/550 W



**Scheme 4** Polymerization reaction mechanism of NVK- TEMABDB-PDS in two phase system

on reaction between multi-site PTC ( $QX_2$ ) and initiator ( $K_2S_2O_8$ ). The generated ( $QS_2O_8$ ) intermediate was aggregating on the interfacial border, where it was decomposed in the presence of temperature/ultrasound condition. Thus produce radical anion react with monomer to form monomer radicals so polymerization occurs with successive addition of monomers.

Applying general principles of free radical polymerization and steady-state hypothesis to radical species, the rate law for this mechanism can be derived [45, 54] as follows:

$$R_p = k_p \left[ \frac{k_d K_3 f}{k_t} \right]^{1/2} [Q^{2+}]_w^{1.0} [S_2O_8^{2-}]_w^{1.0} [M]^1 \quad (11)$$

### 3.12 Analysis of poly (N-vinyl carbazole) (PNVK)

#### 3.12.1 <sup>1</sup>HNMR spectra of poly (N-vinyl carbazole)

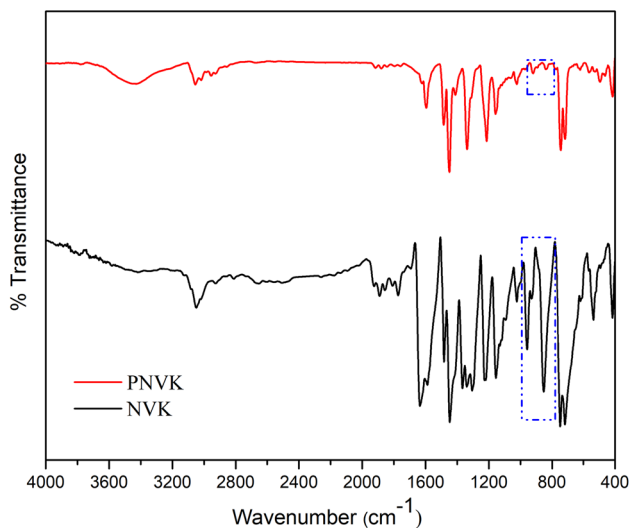
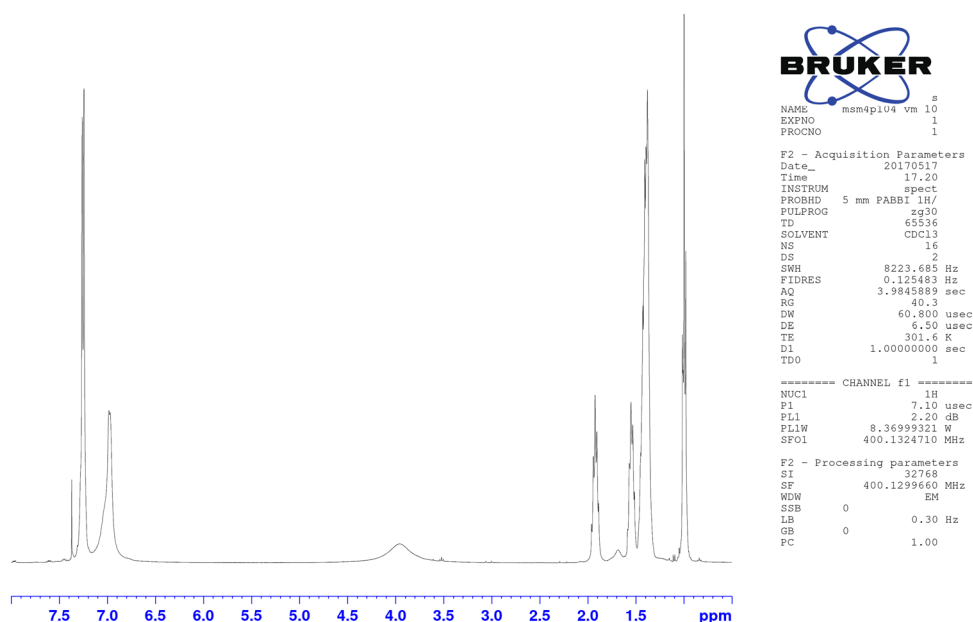
The <sup>1</sup>HNMR spectrum of poly (N-vinyl carbazole) was shown in Fig. 11. <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>, δ): a methylene proton gives the signals between 1.3 to 2.0 ppm and N-CH- protons appear at 3.8 ppm. Aromatic protons are well positioned in the aromatic region of 7.0–7.5 ppm.

The vinyl protons of the monomer did not appear at 5–6 ppm in the polymer spectra. It reveals that polymerization reaction was effectively take place at the vinyl position of the monomer.

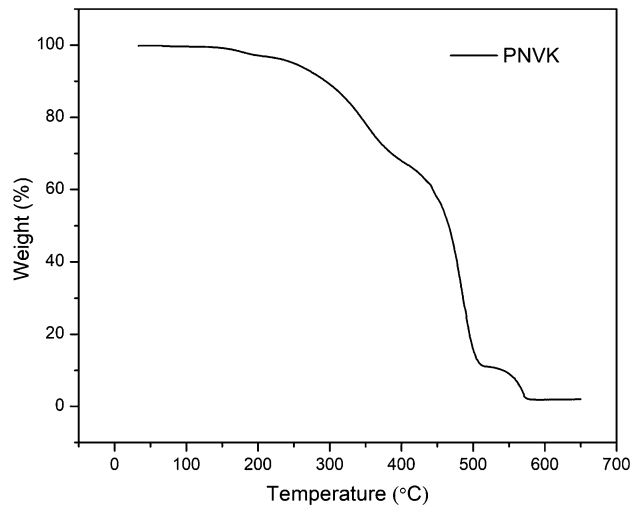
#### 3.12.2 FT-IR analysis of poly (N-vinyl carbazole)

FT-IR spectra of PNVK showed the absence of characteristics stretching band of vinyl group at 852 and



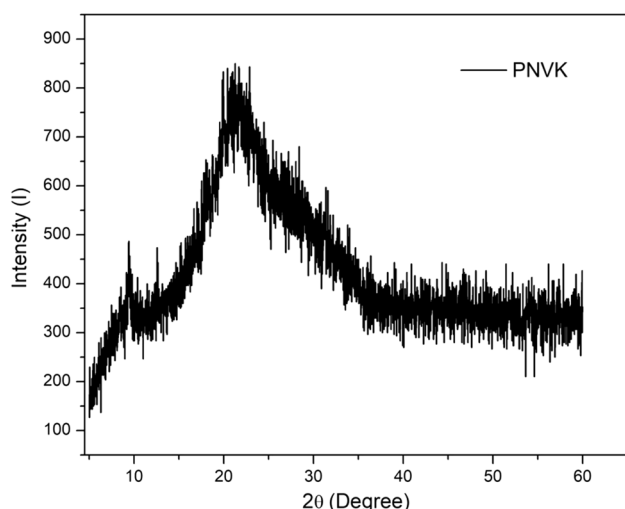
**Fig. 11**  $^1\text{H}$  NMR spectra of the poly (*N*-vinyl carbazole)**Fig. 12** FT-IR spectra of *N*-vinyl carbazole and poly (*N*-vinyl carbazole)

957  $\text{cm}^{-1}$  (Fig. 12) thus confirms that the polymerization takes place selectively through the vinyl groups. The following bands are observed at 2954 and 3054  $\text{cm}^{-1}$  due to aliphatic stretching of  $-\text{CH}$  and  $-\text{CH}_2$  groups. The stretching bands at the range of 1213–1157  $\text{cm}^{-1}$  belongs to out of plane deformation of vinylidene group. In addition to that, a series of bands appeared at 1448 and 1584  $\text{cm}^{-1}$  which are attributed to  $-\text{CH}$  of carbazole ring,  $-\text{C}=\text{C}-$  stretching of aromatic vinylidene groups. A peak at 1337  $\text{cm}^{-1}$  due to  $\text{C}-\text{N}$  bonds and a band at 3054  $\text{cm}^{-1}$  ascribed to the  $=\text{C}-\text{H}$  stretching vibrations of the aromatic ring [55].

**Fig. 13** TGA of poly (*N*-vinyl carbazole)

### 3.12.3 TGA of poly (*N*-vinyl carbazole)

The TG curve of PNVK revealed that the very minute weight loss at 205 °C and loss of weight about less than ten percent weight loss of polymer. The first clear slight weight loss was observed at 227–400 °C with loss of 29.5%. In the second phase polymer showed a weight loss of about 56.5% in the temperature range 401–510 °C. The maximum rate of weight loss appeared around 490 °C. In the third stage PNVK showed a weight loss about 9.0% in the temperature range 511–573 °C and appears due to extensive degradation of the polymer, leaving residue of few percent of the sample weight (Fig. 13). This trend was easily associated with reported TG curve of polymer [56].



**Fig. 14** XRD patterns of poly (*N*-vinyl carbazole)

### 3.12.4 XRD patterns of poly (*N*-vinyl carbazole)

The powder X-ray diffraction (XRD) pattern of PNVK was shown in Fig. 14. The poly (*N*-vinyl carbazole) had a sharp diffraction peak at  $2\theta = 9.22^\circ$  and the polymeric chain distance were found at around  $21.50 \text{ \AA}$ . The broad and diffuse hallow peaks at  $2\theta$  of 18 to  $25^\circ$  of PNVK confirm the amorphous nature of polymer. A similar type of XRD pattern of PNVK was reported under different reaction conditions [57].

## 4 Conclusions

In summary, the polymerization of *N*-vinyl carbazole in two phase system using multi-site phase transfer catalyst and water soluble initiator was successfully accomplished. Indeed, the polymerization rate was effectively doubled with ultrasound on compare with silent polymerization. The various experimental parameters on the polymerization rate were explored and evaluated for both conditions. Rate of polymerization was found to increase with rise of concentration of different variables.  $E_a$  value (activation energy) of polymerization was supported an enhancement of rate under ultrasound condition. The obtained polymer was confirmed and analyzed by various techniques. This investigation exhibits the effective role of ultrasound condition on phase transfer catalyzed polymerization. The combined approach of ultrasound and phase transfer catalyst in the polymerization of various *N*-vinyl monomers may open up new way in the polymerization reactions.

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### Compliance with ethical standards

**Conflict of interest** The authors declare that there is no conflict of interest regarding the publication of this article.

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