

PRIMARY AMINATION AND A NEW METHOD OF QUANTITATIVE ASSESSMENT FOR FIVE FORMING AMINATED STRUCTURES

Nguyen Thi Hieu Ha^{1*}, Hoang Thai Son², Grainne M. Moran³

¹*Institute of Chemistry, Vietnam Academy of Science and Technology*

²*School of Computer Science and Engineering, UNSW, Sydney 2052, Australia*

³*School of Chemistry, UNSW, Sydney 2052, Australia*

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Abstract

The amination of a polymer with a primary amine results in five aminated structures in different proportions: secondary ammonium, secondary amine, cross-linked tertiary ammonium, cross-linked tertiary amine and cross-linked quaternary ammonium. A new quantitative assessment method has been designed and applied for evaluation the five respective individual aminated mole fractions. The method based on a computer program named “*Min SS*” written in Java script which provides the best match of a set of the five individual aminated mole fractions with the experimental determined element weight fractions of four elements C, H, N and Cl constructing the aminated polymer. This is the only method being able to quantitatively analyse the polyvinylbenzylchloride aminated with primary ethylamine in details, because this crosslinked polymer is insoluble for a convenient analysis.

Keywords: “*Min SS*”, aminated mole fraction, element weight fraction.

1. INTRODUCTION

In the amination of polyvinylbenzylchloride (PVBC) containing chloromethylene ($-\text{CH}_2\text{Cl}$) functional groups, with primary (RNH_2) ethyl amine (EtNH_2), there are five types of bonding which can arise at the N-atom. They are secondary ammonium

and amine ($^+\text{N}2^\circ$ and $\text{N}2^\circ$), each bonded with one $-\text{CH}_2\text{Cl}$ group; cross-linked tertiary ammonium and amine ($^+\text{N}3^\circ$ and $\text{N}3^\circ$), each bonded with two $-\text{CH}_2\text{Cl}$ groups; and cross-linked quaternary ammonium ($^+\text{N}4^\circ$) bonded with three $-\text{CH}_2\text{Cl}$ groups of the PVBC polymer.



The product is a mixture of these five ammonium and amine unit structures ($^+\text{N}2^\circ$, $\text{N}2^\circ$, $^+\text{N}3^\circ$, $\text{N}3^\circ$ and $^+\text{N}4^\circ$). Because the crosslinked structures are so often present, the polymers this type are expected not to dissolve in most solvents for a further convenient quantitative analysis. Elemental analysis (EA) is a most suitable method to use for these solid samples, where the weight percentages of element (%E) like N, C and H (%C, %H and %N) can be determined quantitatively. For a pure EtNH_2

aminated PVBC, there is only one more, the fourth element, Cl, constructs the substance. Therefore, from three EA determined weight percentages %C, %H and %N, we can calculate the remaining which is %Cl. Quantitative analysing from these experimental data for the aminated amount is only able for the case if only one of the five reactions, eqs. (1a)–(1e), occurs. If two or more reactions happen, EA data are unable to be used directly for

detailed quantitative assessments on the components of the five aminated structures.

This paper reports a solution for quantitative evaluation of the amounts of the forming aminated structures in these polymers. The solution bases on a computer program, named “*Min SS*”. It is designed to estimate the best matched values of sets of the individual aminated mole fractions (a_1, a_2, a_3, a_4 and a_5) of the five respective aminated structures with the EA determined weight fractions of $wf_{N, exp}$, $wf_{C, exp}$, $wf_{H, exp}$ and $wf_{Cl, exp}$. That is very *useful in estimating the structures of insoluble polymers*, and is also the only method being able to quantitatively analyse these polymers in present. Quantitative potential analysis methods for structures like solution NMR or MS are unable to apply for the crosslinked polymers. Even for a soluble polymer with many structures constructed, these methods can only be applied in limited cases for detailed analysing the individual structures.

2. EXPERIMENTAL

2.1. Amination

Poly(4-vinylbenzyl chloride) (Aldrich) (PVBC) ($[-CH_2-CH(C_6H_4-CH_2Cl)]_{dp-}$, $\overline{M}_n = 55\ 000$ g/mol, $dp \approx 360$, $\overline{M}_w = 100\ 000$ g/mol (GPC), $\overline{M}_w/\overline{M}_n = 1.82$); Ethylamine (2 M in THF, Aldrich) ($EtNH_2$) with d (2M solution in THF) = 0.783 g/ml ($C_2H_5NH_2 = 45.09$ g/mol, mp -81 °C, bp 16.6 °C); Tetrahydrofuran (99 %, Unichrom APS Ajax Finchem) (THF) ($C_4H_8O = 72.1$ g/mol, mp $-108 - 66$ °C, bp 65 °C, d 0.889 g/ml, ϵ 7.6) and Methanol (99.7 %, UniChrom APS Ajax Fine Chemical) ($CH_3OH = 32.04$ g/mol, mp -97.7 °C, bp 65 °C, d 0.787 g/ml, ϵ 32.7) were used as supplied.

The amination reaction was carried out in a stopped glass tube which was shaken in a temperature controlled water bath. Polymer unit concentrations ([p.u.]) varied from 0.16-0.50 M, while the amine concentration was twice that of the [p.u.]. The reaction time varied from 3-24 h. The temperature was set to 22 ± 2 °C, 40.0 ± 0.2 °C or 60.0 ± 0.2 °C. THF solvents dissolved the polymer and amine quite well at the beginning, but the reaction mixture turned slightly heterogenous very quickly due to the newly formed ionic bonding following the reaction of the chloromethylene group ($-CH_2Cl$) and the amine. Ethylamine aminated polymer products were precipitated in methanol. They were then collected on a sinter glass funnel G4 and washed several times with methanol under

reduced pressure facilitated by a water aspirator pump (> 100 mmHg). Finally, the polymer was dried in a glass desiccator under vacuum at room temperature till the weight stayed constant (around 6 – 20h).

2.2. Elemental analysis (EA)

The microanalyses of the polymer samples were carried out on an Elemental Analyzer E.A. 1108 (Carlo Erba TM Instruments) [1, 2]. The determination of N, C and H is based on the gas chromatogram of a gas mixture converted from the powder sample by quantitative *dynamic flush combustion*. A small amount of polymer sample (2–3 mg) was weighed by a high precision Perkin Elmer TM auto-balance ($\pm 10^{-7}$ g) in a tin capsule. It was then placed in the auto-sampler of the apparatus. The experiment was automatically run and monitored by computer software Eager®. The sample was firstly dropped and burned in a combustion tube quantitatively and further oxidised by oxygen in a following column of chromium oxide (Cr_2O_3) and Ag/ cobaltous-Co oxide to nitrogen oxides (NO_x), carbon dioxide and water vapour at 1020 °C, catalytically. This mixture of gases is then passed over a special fine grain copper column to remove the excess O_2 and to reduce NO_x to elemental nitrogen (N_2) at 650 °C. Then it is directed to the chromatographic column (porapak PQS) operated at 60 °C where the individual components were separated and eluted as N_2 , CO_2 and H_2O by carrier gas He. A *thermal conductivity detector* provides the signals which are processed by an integration program in comparison with a calibrated chromatogram of a standard compound (acetanilide, $CH_3CONH(C_6H_5) = C_8H_9ON = 135.166$ g/mol) and that of a “blank” sample (empty tin capsule). As the result, the weight percentages can be read from the printout. The analysis was repeated two or three times for each sample. The uncertainties of the element weight percentage (%E) abstracted from previous routine work are ± 0.07 , ± 0.15 and ± 0.22 for %C, %H and %N, respectively [2].

The K-factor method was used to calculate the elemental weight percentages where:

$$K = \frac{w_{std.} \times \%E_{std.}}{A_{std.} - A_{blank}} \quad (2)$$

$$\%E_{sample} = \frac{K \times (A_{sample} - A_{blank})}{w_{sample}} \quad (3)$$

with $w_{std.}$, w_{sample} = weight of standard compound and of sample, respectively.

$\%E_{std.}$ = weight percentage of element E in standard compound (In case of acetanilide $\%C_{std.} = 71.089$,

$\%H_{std.} = 6.712$, $\%N_{std.} = 10.363$, $\%O_{std.} = 11.837$)

E = element N, C or H.

$\%E_{sample}$ = weight percentage of element E in sample

$A_{std.}$, A_{blank} , A_{sample} = peak areas of element E of standard, blank and unknown sample.

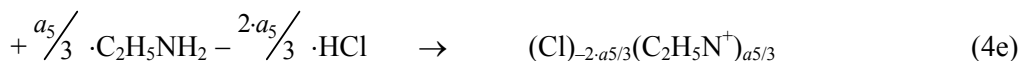
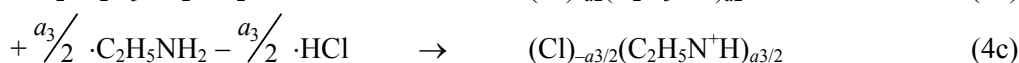
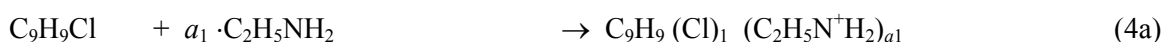
3. COMPUTER PROGRAM “Min SS”

The program was designed particularly to evaluate the composition of the five individual aminated mole fractions ($a_1 - a_5$). Although it serves the data processing, which may be part of the Experimental part; But because it is the key complex

solution, the principles of the program design are assembled in this separate part.

In the amination of PVBC with primary EtNH₂, five reactions are expected to involve to form the five different ammonium and amine structures with the formula of an average polymer unit $C_9H_9Cl \rightarrow (CH)_9Cl_{1-0}(C_2H_5NH_{2-0})_{a=0-1}$, deduced as seen in scheme 1, eqs. (4a)–(4e). See eqs. (1a)–(1e) respectively for conversions.

The element weights (N, C, H, Cl) and weight fractions ($wf_N, wf_C, wf_H, wf_{Cl}$) in an average polymer unit of the PVBC aminated with EtNH₂ are shown in scheme 2. These calculations are derived from the formula reactions, eqs. (4a)–(4e).



The total aminated mole fraction a ranges: $0 \leq (a = a_1 + a_2 + a_3 + a_4 + a_5) \leq 1$ (5)

Scheme 1: Reactions scheme with formula of an average polymer unit in the amination of PVBC with EtNH₂, $C_9H_9Cl \rightarrow (CH)_9Cl_{1-0}(C_2H_5NH_{2-0})_{a=0-1}$. That results in five ammonium and amine unit structures ($^+N2^0, N2^0, ^+N3^0, N3^0$ and $^+N4^0$) with the respective aminated mole fractions a_1, a_2, a_3, a_4 and a_5

$$N = 14.007 \cdot (a_1 + a_2 + \frac{a_3}{2} + \frac{a_4}{2} + \frac{a_5}{3}) \quad wf_{N,calc} = \frac{N}{M(p.u.)} \quad (6) \text{ and } (6a)$$

$$C = 12.011 \cdot (9 + 2 \cdot a_1 + 2 \cdot a_2 + a_3 + a_4 + \frac{2 \cdot a_5}{3}) \quad wf_{C,calc} = \frac{C}{M(p.u.)} \quad (7) \text{ and } (7a)$$

$$H = 1.008 \cdot (9 + 7 \cdot a_1 + 6 \cdot a_2 + 3 \cdot a_3 + 2.5 \cdot a_4 + \frac{5 \cdot a_5}{3}) \quad wf_{H,calc} = \frac{H}{M(p.u.)} \quad (8) \text{ and } (8a)$$

$$Cl = 35.453 \cdot (1 - a_2 - \frac{a_3}{2} - a_4 - \frac{2 \cdot a_5}{3}) \quad wf_{Cl,calc} = \frac{Cl}{M(p.u.)} \quad (9) \text{ and } (9a)$$

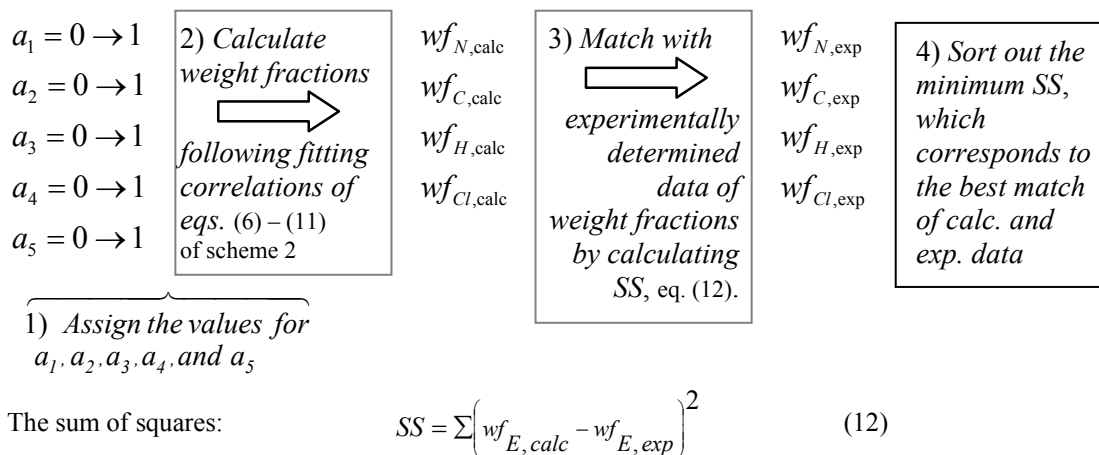
$$M(p.u.) = N + C + H + Cl \quad \sum wf_E = 1 \quad (10) \text{ and } (10a)$$

$$M(p.u.) = 152.624 + 45.085 \cdot a_1 + 8.624 \cdot a_2 + 4.321 \cdot a_3 - 13.919 \cdot a_4 - 9.279 \cdot a_5 \quad (11)$$

Scheme 2: The element weights (N, C, H, Cl) and weight fractions ($wf_N, wf_C, wf_H, wf_{Cl}$) in an average polymer unit of the PVBC aminated with EtNH₂. The deductions is made from eqs. (4a)–(4e), presented in scheme 1

The program “Min SS” was written in Java language. It has four major steps sketched out in scheme 3 where a single solution is provided in data processing. The sum of squares (SS) between the calculated and the experimental data is a typical variable demonstrating a deviation of the ascribed theoretical correlations with the practicing observations [3]. The programming for a minimum

SS have been used in curve fit for series of data of triad mole fractions and composition of copolymers [4, 5 and cited refs.]. It has been composed in Fortran with different programming principles. The Min SS program used in this report has been specially designed to process the experimental weight fractions of elements constructing the polymer.



Scheme 3: Sketch of major steps of the program “Min SS”

In the first step: a set of 5 values from 0 to 1 are assigned for 5 variables a_1, a_2, a_3, a_4 and a_5 with a restriction expressed by eq. (5). This set of the values are then used to calculate the respective weight fractions $wf_{N,calc.}, wf_{C,calc.}, wf_{H,calc.}$ and $wf_{Cl,calc.}$, using eqs. (6)–(9a) and (10). In the third step: the sum of squares (SS) of the deviations between the calculated $wf_{E,calc.}$ and the experimental determined $wf_{E,exp.}$ is calculated by eq. (12) for all four elements. In the final steps, all the SS values calculated from all the sets of the value assigned variables a_1, a_2, a_3, a_4 and a_5 are sorted out for the minimum. The determined “min SS value” will indicate the best match values of aminated mole fractions a_1, a_2, a_3, a_4 and a_5 with the EA

experimental data. As we may notice the EA data is the initial source of this data analysis process.

4. RESULTS AND DISCUSSION

The preparation conditions of the five ethylaminated PVBC are shown in table 1. The samples were analysed by EA for the experimental data of the element weight percentage of nitrogen (%N), carbon (%C) and hydrogen (%H), see Tab. 1. The chloro weight percentage (%Cl) is calculated with the assumption that there is no oxygen or any other contamination, in which %N, %C and %H are subtracted from 100 %.

Table 1: Amination of PVBC ($dp \approx 360, M_n = 55\,000 \text{ g.mol}^{-1}$) with ethylamine in THF

g (PVBC)	ml (amine)	ml (THF)	[p.u.] in M	Σ ml	T (°C)	t_{reaction} in h	g (product)	Name of product	EA (exp.)			
									%N	%C	%H	%Cl
1	6.5	12.5	0.328	20	60	3	0.930	Q2PVBC	1.94	74.89	7.06	16.11
1.001	6.5	12.5	0.328	20	40	22.64	0.921	Q2PVbd	3.13	78.45	7.95	10.47
0.503	3.25	6.25	0.328	10	22	12	0.488	Q2PVBe	1.67	73.79	7.04	17.50
0.498	3.25	6.25	0.328	10	22	24	0.479	Q2PVbf	2.02	75.17	7.35	15.46
0.5	3.25	16.25	0.164	20	22	24.17	0.472	Q2PVBg	1.14	76.52	6.66	15.07

[p.u.] = concentration of an average polymer unit ($C_9H_9Cl = 152.624 \text{ g/mol}$)

[amine] = 2[p.u.]

Σ ml = total reaction volume in ml

T(°C) = reaction temperature with fluctuation observed to be $\Delta T = \pm 0.2$ at 60 and 40°C and ± 2.0 at 22°C

%N, %C and %H are determined by EA; $\%Cl = 100 - \%N - \%C - \%H$.

If only one of the five reactions, eqs. (1a)–(1e), happens, the total aminated mole fraction of these five reactions (a) is equal to one of the five individual corresponding mole fractions a_1, a_2, a_3, a_4 or a_5 . Scheme 4 shows the formulae of the a_1, a_2, a_3, a_4 and

a_5 calculated from the weight fractions ($wf_{E,exp.}$) for four elements N, C, H and Cl in each reaction ($a_{1C}, a_{1H}, a_{1Cl}, a_{1N}, \dots, a_{5N}$). The five reactions presented in the scheme express for an average polymer unit $C_9H_9Cl \rightarrow (CH)_9Cl_{1-0}(C_2H_5NH_{2-0})_{a-0-1}$, derived from

eqs. (1a)–(1e) correspondingly.

Theoretically, in this case, the aminated mole fractions calculated from $wf_{C,exp}$, $wf_{H,exp}$, $wf_{Cl,exp}$ and $wf_{N,exp}$ should equal to each other which correspond to the only happening reaction. That means, e.g., when only the forming of $^+N2^0$ bonding progresses, eq. (1a), $a_{1C} = a_{1H} = a_{1Cl} = a_{1N} = a_1 = a$. In a real case, that is almost never in expectation. The 20 values of individual aminated mole fractions (a_{1C} , a_{1H} , a_{1Cl} , a_{1N} , ..., a_{5N} , see scheme 4), have 20 different values. The wide range of the “a” values, e.g., $a_{1-5,N} = 0.214-0.611$ (a_{1N} , a_{2N} , a_{3N} , a_{4N} and a_{5N}) calculated from EA determined $wf_{N,exp}$, for 5 reactions, for sample Q2PVBC (see Tab. 2) strongly suggest all the five reactions (eqs. (1a)–(1e)) happen at different levels. Processing data using scheme 4 is a labourous and tiring work with not much conclusions; It is used as a test if the case of only one reaction presents.

Table 2 collates the best matched values of five aminated mole fractions a_1 , a_2 , a_3 , a_4 and a_5 calculated by the program *Min SS* for the experimental data of weight fractions of the four constructing elements N, H, C and Cl of the PVBC aminated with ethylamine. The sums of squares of these best matches, *min SS*, range from 10^{-6} – 10^{-4} . That is well lower than the EA experimental uncertainties of the weight fractions $\Delta wf_{E,exp} =$

± 0.005 . That implies a good quality of the matching process run by the program *Min SS*. Mathematically, in the amination with primary amine, the solution for five variables $a_1 - a_5$ from the calculations based on four correlations expressed by equations (6)–(9) is unlimited ($5 > 4$, 4 correlations of 5 variables). Value assignment process follows in order from the variable $a_1 - a_5$. That is prioritising the order of the five reactions from forming secondary ammonium ($^+N2^0$), eq. (1a), (as the highest priority) to forming quaternary ammonium ($^+N4^0$), eq. (1e), (as the lowest priority) in data processing.

As can be seen in Tab. 2, with the reaction at 40°C over 22.64 h and with the concentration of VBC units in the initial mixture [p.u.] = 0.328 M, the sample Q2PVBd has the highest mole fraction of aminated VBC units in linear poly(VBC) ($a_{1-5,N} = 0.348-0.963$). This coincides with the highest EA determined %N = 3.13% and the highest total amination mole fraction evaluated by program *Min SS* ($a = 0.89$) observed among the five aminated products. The evaluated value of a in the range of $a_{1-5,N}$ indicates the reliability of the “a” data provided by program *Min SS*. Quaternary ammonium ($^+N4^0$) bonding is over dominant (greatest $a_5 = 0.73$) among the five companions. The ammonium bonding overweighs the amine ($a_{1+3+5} = 0.85$, $a_{2+4} = 0.04$).

Table 2: The best matched values of five aminated mole fractions (a_1, a_2, a_3, a_4 and a_5)^{b)} calculated by the program “*Min SS*” for the experimental data of weight fractions of the four constructed elements N, H, C and Cl of the PVBC aminated with ethylamine. The sums of squares of the best matches, *min SS*, range from 10^{-6} – 10^{-4}

[p.u.] in M	T (°C)	$t_{reaction}$ in h	Name of product	%N (EA)	$a_{1-5,N}$ ^{a)}	a_1 $^+N2^0$	a_2 $N2^0$	a_3 $^+N3^0$	a_4 $N3^0$	a_5 ^{b)} $^+N4^0$	a_{1+3+5} $^+N^c)$	$+ a_{2+4}$ $N^d)$	= a
0.328	60	3	Q2PVBC	1.94	0.214-0.611	0.02	0.04	0.12	0.17	0.06	0.2	0.21	0.41
0.328	40	22.64	Q2PVBd	3.13	0.348-0.963	0.06	0.02	0.06	0.02	0.73	0.85	0.04	0.89
0.328	22	12	Q2PVBe	1.67	0.184-0.528	0.02	0.05	0.15	0.09	0.04	0.21	0.14	0.35
0.328	22	24	Q2PVBf	2.02	0.223-0.635	0.06	0.02	0.04	0.03	0.40	0.5	0.05	0.55
0.164	22	24.17	Q2PVBg	1.14	0.125-0.364	0.01	0.01	0.01	0.01	0.49	0.51	0.02	0.53

^{a)} $a_{1-5,N}$ = the aminated mole fraction range ($a_{1N}, a_{2N}, a_{3N}, a_{4N}$ and a_{5N}) calculated from $wf_{N,exp}$ (scheme 4), assuming for the case if only one of five reactions, eqs. (1a)–(1e), happens.

^{c)} ^+N = ammonium structures $^+N2^0, ^+N3^0$ and $^+N4^0$; a_{1+3+5} is aminated fraction of these ammonium structures.

^{d)} N = amine structures $N2^0$ and $N3^0$; a_{2+4} is aminated fraction of these forming amine structures.

Higher temperature of 60 °C possibly quickly creates much more crosslinks which hinder the amination to progress effectively, sample Q2PVBC, that the total aminated unit only show a mole fraction around 0.41. The largest amount of the aminated structure is seen for the cross-linked

tertiary amine ($N3^0$), where $a_4 = 0.17$ is the greatest value among the five companions.

Low temperature of 22 °C provide relatively low aminated mole fraction ($a = 0.35-0.55$) in samples Q2PVBe, Q2PVBf and Q2PVBg. That indicates the amination in this low temperature is not very

Scheme 4: Calculation of the mole fraction of aminated units (a) in the PVBC aminated with ethylamine from the elemental analysed weight fractions of N, C and H; assuming that *only one type of bonding at N-atom was formed*. The five formula reactions presented in the scheme express for an average polymer unit $\{C_9H_9Cl \rightarrow (CH)_9 Cl_{1-0} (C_2H_5NH_{2-0})_{a=0-1}\}$ derived from eqs. (1a)–(1e) correspondingly

$(CH)_9 Cl_1$ + $a_1 (C_2H_5NH_2) \rightarrow$ <u>$(CH)_9Cl (C_2H_5NH_2)_{a1} (^+N2^0)$</u>	$(CH)_9 Cl_1$ + $a_2 (C_2H_5NH_2) - a_2 HCl \rightarrow$ <u>$(CH)_9Cl_{1-a2} (C_2H_5NH)_{a2} (N2^0)$</u>	$(CH)_9 Cl_1$ + $(a_3/2)(C_2H_5NH_2) - (a_3/2) HCl \rightarrow$ <u>$(CH)_9Cl_{1-0.5a3} (C_2H_5NH)_{0.5a3} (N3^0)$</u>	$(CH)_9 Cl_1$ + $(a_4/2) (C_2H_5NH_2) - a_4 HCl \rightarrow$ <u>$(CH)_9Cl_{1-a4} (C_2H_5N)_{0.5 a4} (N3^0)$</u>	$(CH)_9 Cl_1$ + $(a_5/3) (C_2H_5NH_2) - (2a_5/3) HCl \rightarrow$ <u>$(CH)_9Cl_{1-(2a5/3)} (C_2H_5N)_{(a5/3)} (N4^0)$</u>
$C = 12.011 \cdot (9 + 2a_1)$	$C = 12.011 \cdot (9 + 2a_2)$	$C = 12.011 \cdot (9 + a_3)$	$C = 12.011 \cdot (9 + a_4)$	$C = 12.011 \cdot [9 + (2a_5/3)]$
$H = 1.008 \cdot (9 + 7a_1)$	$H = 1.008 \cdot (9 + 6a_2)$	$H = 1.008 \cdot (9 + 3a_3)$	$H = 1.008 \cdot (9 + 2.5a_4)$	$H = 1.008 \cdot [9 + (5a_5/3)]$
$Cl = 35.453$	$Cl = 35.453 \cdot (1 - a_2)$	$Cl = 35.453 \cdot (1 - 0.5a_3)$	$Cl = 35.453 \cdot (1 - a_4)$	$Cl = 35.453 \cdot [1 - (2a_5/3)]$
$N = 14.007 a_1$	$N = 14.007 a_2$	$N = 14.007 (a_3/2)$	$N = 14.007 (a_4/2)$	$N = 14.007 (a_5/3)$
<u>$\overline{M(p.u.)} = 152.624 + 45.085 a_1$</u>	<u>$152.624 + 8.624 a_2$</u>	<u>$152.624 + 4.321 a_3$</u>	<u>$152.624 - 13.919 a_4$</u>	<u>$152.624 - 9.279 a_5$</u>
$a_{1C} = \frac{[wf_C \cdot 12.707 - 9] = N_C}{2 - wf_C \cdot 3.754}$	$a_{2C} = \frac{N_C}{2 - wf_C \cdot 0.718}$	$a_{3C} = \frac{N_C}{1 - wf_C \cdot 0.36}$	$a_{4C} = \frac{N_C}{1 + wf_C \cdot 1.159}$	$a_{5C} = \frac{N_C}{(2/3) + wf_C \cdot 0.773}$
$a_{1H} = \frac{[wf_H \cdot 151.412 - 9] = N_H}{7 - wf_H \cdot 44.73}$	$a_{2H} = \frac{N_H}{6 - wf_H \cdot 8.556}$	$a_{3H} = \frac{N_H}{3 - wf_H \cdot 4.287}$	$a_{4H} = \frac{N_H}{2.5 + wf_H \cdot 13.809}$	$a_{5H} = \frac{N_H}{(5/3) + wf_H \cdot 9.205}$
$a_{1Cl} = \frac{[x - wf_{Cl} \cdot 4.305] = N_{Cl}}{wf_{Cl} \cdot 1.272}$	$a_{2Cl} = \frac{N_{Cl}}{1 + wf_{Cl} \cdot 0.243}$	$a_{3Cl} = \frac{N_{Cl}}{0.5 + wf_{Cl} \cdot 0.122}$	$a_{4Cl} = \frac{N_{Cl}}{1 - wf_{Cl} \cdot 0.393}$	$a_{5Cl} = \frac{N_{Cl}}{(2/3) - wf_{Cl} \cdot 0.262}$
$a_{1N} = \frac{[wf_N \cdot 10.897] = N_N}{1 - wf_N \cdot 3.219}$	$a_{2N} = \frac{N_N}{1 - wf_N \cdot 0.616}$	$a_{3N} = \frac{N_N}{0.5 - wf_N \cdot 0.308}$	$a_{4N} = \frac{N_N}{0.5 + wf_N \cdot 0.994}$	$a_{5N} = \frac{N_N}{(1/3) - wf_N \cdot 0.662}$
Theoretically, $a_1 = a_{1C} = a_{1H} = a_{1Cl} = a_{1N}$	$a_2 = a_{2C} = a_{2H} = a_{2Cl} = a_{2N}$	$a_3 = a_{3C} = a_{3H} = a_{3Cl} = a_{3N}$	$a_4 = a_{4C} = a_{4H} = a_{4Cl} = a_{4N}$	$a_5 = a_{5C} = a_{5H} = a_{5Cl} = a_{5N}$

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C, H, Cl and N = mol. wt. of element C, H, Cl and N in an average aminated polymer unit, respectively.

$M(p.u.)$ = mol. wt. of an average aminated polymer unit.

Weight fraction of element $wf_E = \%E : 100$, where $E = C, H, Cl$ or N . ($wf_C + wf_H + wf_{Cl} + wf_N = 1$).

According to the correlation " $wf_E = E / M(p.u.)$ ", the a_E can be deduced individually for each case as demonstrated above ($a_{1C}, a_{1H}, a_{1Cl}, a_{1N}, \dots, a_{5N}$: 20 values in total).

$0 \leq a \leq 1$. The actual total mole fraction of aminated units a is the sum of five individual aminated fractions ($a = a_1 + a_2 + a_3 + a_4 + a_5$).

When only one reaction presents, the a equal the one of the respective a_1, a_2, a_3, a_4 or a_5 .

effective. Longer reaction time (24 h, Q2PVBf compares with 12 h, Q2PVBe) resulting in better amination portion: ($a_{Q2PVBf} = 0.55$) > ($a_{Q2PVBe} = 0.35$). Dilute reactant concentration ($[p.u.] = 0.164$, Q2PVBg) and long reaction time ($t_{\text{reaction}} = 24.17$ h) seems to promote the high portion of the forming of the cross-linked quaternary ammonium bonding ($^+N4^0$), where $a_5 = 0.49$ is the greatest among 15 individual aminated mole fractions listed for these three polymers prepared at 22 °C.

5. CONCLUSIONS

New method of data assessments for the individual aminated unit mole fractions (a_1, a_2, a_3, a_4 and a_5) of the respective forming secondary ammonium ($^+N2^0$), secondary amine ($N2^0$), cross-linked tertiary ammonium ($^+N3^0$), cross-linked tertiary amine ($N3^0$) and cross-linked quaternary ammonium ($^+N4^0$) structures in a primary amination has been designed and thorough investigated. The method bases on the computer program, named “*Min SS*”. It is designed to estimate the best matched values of a set of the 5 variables a_1, a_2, a_3, a_4 and a_5 with the EA experimental determined weight fractions of $wf_{N, \text{exp}}, wf_{C, \text{exp}}, wf_{H, \text{exp}}$ and $wf_{Cl, \text{exp}}$. Good agreements have been observed for five samples of polyvinylbenzylchloride aminated with ethylamine.

In regular present working conditions, that is the only method being capable to quantitatively analyse these crosslinked insoluble polymers in details.

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Corresponding author: **Nguyen Thi Hieu Ha**

Institute of Chemistry,
Vietnam Academy of Science and Technology
18 Hoang Quoc Viet Rd., Cau Giay District, Hanoi, Vietnam
Email: hanth262@gmail.com; Tel.: 0169 380 4460.