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Development of Poly(ethylene glycol) Based Amphiphilic Copolymers for Controlled Release Delivery of Carbofuran

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The formation of micelles in a solvent that is selective for one of the blocks is one of the most important and useful properties of block copolymers. We had synthesized copolymers of polyethylene glycol and various dimethyl esters, which self assemble into nano micellar aggregates in aqueous media. In the present work, we have utilized these nano micelles for the encapsulation of carbofuran, [2,3–dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate], a systemic insecticide-nematicide, for the development of controlled release formulation.

Keywords: Diester copolymers, self assembly, controlled release, carbofuran

1 Introduction

The unique properties of poly(ethylene glycol) (PEG), including a wide range of solubility, lack of toxicity, non-interference with enzymatic activities and conformations of polypeptides and ease of excretion from living organisms, make them ideal drug carriers (1). The two hydroxyl-end groups of PEG have been suitably functionalized prior to coupling (2) with ligands of biological relevance, although the hydroxyl groups themselves have been used as well (3–5). Because the number of terminal groups of PEGs (only two) to attach with drug limits their drug loading capacity, extensive work has been done to functionalize them by copolymerizing PEGs with various functional monomers. Amphiphilic block copolymers with hydrophilic and hydrophobic segments have been investigated extensively not only because of their unique self-organization characteristics but also for their wide range of potential applications, such as in drug delivery and separation technology systems (6). The micellar characteristics of amphiphilic block copolymers depend on the nature of each block and surface properties of self-organized micelles are highly dependent on the structures of the hydrophilic blocks (7–9).

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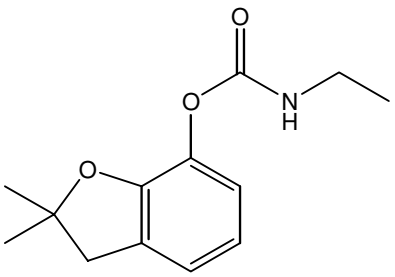
Earlier, we reported the synthesis and self assembly of copolymers derived from PEGs and diester (10–13) and their use in drug delivery systems capable of encapsulating both hydrophilic and hydrophobic drugs (14–15). This approach is based on the formation of nano-micelles by the self-assembly of amphiphilic copolymers in aqueous media. The amphiphilic polymers used in the self-assembly are based on poly(ethylene glycol) and various diesters, synthesized by chemical and enzymatic methods (12–13). The design of the system and synthetic strategy is very flexible and provides a high degree of control over the polymer structures. This allowed the tuning of the properties of the micelle disruption, the critical micelle concentration and the size of micelles.

In the present study, we have extended the work to encapsulate pesticides, e.g. carbofuran, for the development of controlled release formulation. There have been reports in literature where commercially available polymers have been utilised for the development of controlled release formulations of different pesticides (16–17). However, there is no report whatsoever where amphiphilic nanopolymers have been used for the development of controlled release formulations.

Carbofuran [2,3–dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate], is a systemic insecticide-nematicide for soil and foliar treatments. Being a carbamate it inhibits the cholinesterase enzyme and inactivates the nervous system



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(18–19). Because of its great potential, it is widely used for the control of insects in several field crops. In order to achieve control of insects, it is necessary to maintain an appropriate concentration of chemicals in contact with the plants for a sufficient amount of time for absorption to take place. To counter environmental losses and maintain the concentration above the minimum threshold of activity, application of excessive amount of conventional formulation of carbofuran is required. Increase in application rate, however, is likely to increase the potential adverse impact on the environment. The excessive quantities added increase the likelihood of runoff or leaching and thus the pollution of surface or ground water (20). It has been identified as potential leacher by using the groundwater ubiquity score (GUS) modeling technique (21). In addition, carbofuran is of environmental concern because of its high acute toxicity (LD_{50}rat, 8 mg Kg^{-1}) (22).

The danger posed to the environment by current pesticide usage can be reduced by improved pest control practices including systems that provide an amount of active ingredient (a.i.) needed actually to obtain adequate pest control. Controlled release pesticide technology has received increasing attention for the last two decades, due to a growing awareness that pesticides may produce undesirable environmental effects when applied in conventional formulations at the levels required for adequate activity (23). The use of controlled release (CR) formulations can in many cases, supply the a.i. at the required rate and thus reduce the amount of chemical needed for pest control, thereby protecting the environment from the deleterious effects of the pesticides. These permit safer, efficient and economical crop protection, reduce phytotoxicity, degradation, leaching and chemical load in the environment, enable convenient handling and distribution and an extended release period of chemicals. Due to the various advantages, numerous examples are available in literature wherein such products have been effectively employed to combat pests in developed countries (24–26).

In the present study, we demonstrate the encapsulation of carbofuran in nanospheric micelles prepared by enzymatic copolymerization of PEGs of different molecular weights and dimethyl 5-hydroxyisophthalate using Novozyme-435 in bulk. Further, these polymers have been derivatised by attaching decanyl and 12-hydroxydodecanyl chains to the phenolic hydroxyl groups. The present study utilizes the decanyloxy derivative of amphiphilic copolymers **7a-7d** to develop controlled release formulations of carbofuran. This is perhaps the first report where nanopolymers have been used for the development of controlled release formulation of a pesticide.

2 Experimental

2.1 Materials

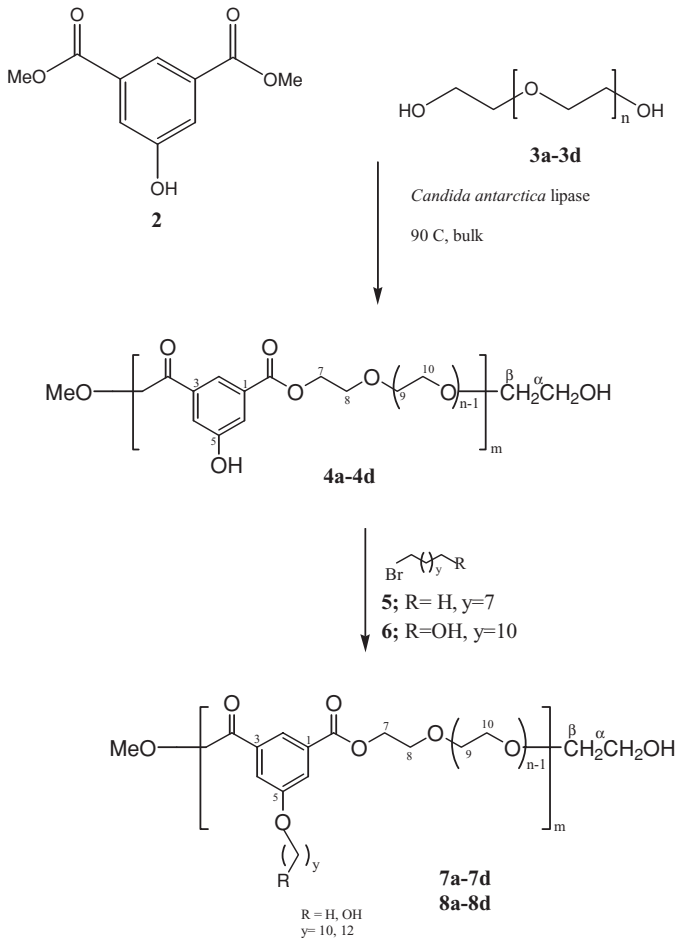
PEG-based amphiphilic polymers were enzymatically synthesized with dimethyl 5-hydroxyisophthalate as linker molecule as reported earlier (Scheme 1) (10). The numbers 600, 900, 1500 and 1800 represent the number average molecular weights of PEG blocks, respectively which were used to form the main molecular chains of the copolymers. The characterization of the polymers was done by ^{1}H and ^{13}C-NMR spectra as reported earlier (10). Novozyme – 435, an immobilized enzyme, was a gift from Novozymes, Denmark. All other chemicals and solvents were of analytical grade and were used as received unless otherwise noted. Carbofuran (Technical Grade) with purity of 85% w/w and commercial granules 3G (3% a.i.) were obtained from its manufacturer M/S Rallis India Ltd., Bangalore, India.

2.2 General Method of Polymerization

Dimethyl 5-hydroxyisophthalate (**2**, 1.0 mmol, 0.21 g) and PEG [**3a-3d**, 1.0 mmol, MWt 600 (0.6 g), 900 (0.9 g), 1500 (1.5 g) and 1800 (1.8 g)] were placed in a round-bottom flask (25 mL capacity). To this mixture was added the enzyme (10% by weight w.r.t. monomers, 0.80 g – 2.01 g) and reaction flask was then placed in a constant temperature oil bath maintained at 90°C under vacuum. The reaction was allowed to proceed for 48h, after this time it was quenched by adding chloroform and filtering off the enzyme under vacuum (Scheme 1). The organic solvent was then evaporated under vacuum and the residue was dialyzed using membrane (MWCO 10000). After the completion of dialysis, the product polymers **4a-4d** were freeze-dried. The structures of the polymers were characterized using NMR spectroscopy (Bruker 250 MHz); and the molecular weights of the polymer products were determined by GPC/light scattering as reported earlier. The spectral data of one representative example of polymers is reproduced below.

2.3 General Method of Coupling of Bromodecane (5) and 12-Bromododecanol (6) with Poly[Poly(Oxyethylene-600)-Oxy-5-Hydroxyisophthaloyl]

Equimolar quantities of **4a–4d** (0.8, 1.1, 1.7 and 2.0 g) and **5** or **6** (0.22 or 0.26 g) were dissolved in dry acetone (10 mL) and to the resultant solution was added equimolar



Scheme 1. General method of polymerization.

amount of anhydrous potassium carbonate (0.13 g). The reaction mixture was refluxed at 60°C and the progress of the reaction was monitored by TLC using ethyl acetate in petroleum ether (30%). After completion, potassium carbonate was removed by filtration and the solvent was removed under vacuum to give the products **7a–7d** and **8a-8d** from **5** and **6**, respectively.

2.3.1. *Polyvinyl chloride*

The polymer (9.645 g), and carbofuran (0.355 g, 85 % purity) were dissolved in a compatible organic solvent. The solution was thoroughly mixed with a metal spatula. The slurry so formed was dried in a Petri dish to yield a hard mass which after drying was ground in a laboratory Wiley mill and then sieved to obtain granules of size 30/60-mesh size.

2.3.2. *Poly[poly(oxyethylene-600)-oxy-5-hydroxyisophthaloyl]* **4a**

This polymer was obtained by heating dimethyl 5-hydroxyisophthalate (1 mmol, 0.21 g) with PEG 600 (1 mmol, 0.6 g) in the presence of Novozyme-435 (0.8 g) at 90°C in solvent free conditions for 48 h under vacuum. It was obtained as a viscous oil after freeze-drying in 90% yield.

^{1}H-NMR Data ($CDCl_3$): δ 3.64–3.68 (*brs*, methylene PEG protons on C-9 and C-10 carbons of the repeating units and on C-α and C-β), 3.82 (*t*, 2H, C-8H), 3.93 (*s*, 3H, -$COOCH_3$), 4.48 (*t*, 2H, C-7H), 7.71 (*m*, 2H, C-4H and C-6H) and 8.21 (*s*, 1H, C-2H).

^{13}C-NMR Data ($CDCl_3$): δ 52.74 (-OCH_3 end group), 62.07 (C-α), 64.74 (C-β), 69.44 (C-8), 70.93 (repeating PEG units' carbons), 72.90 (C-7), 121.43 (C-4 and C-6), 122.53 (C-2), 131.18 (C-1 and C-3), 157.57 (C-5) and 166.11 (-COOMe).

2.3.3. *Poly[poly(oxyethylene-600)-oxy-5-decanyloxyisophthaloyl]* **7a**

^{1}H-NMR Data ($CDCl_3$): δ 0.86–0.92 (*bs,* 3H, C-20H), 1.27–1.38 (*m*,C-13H to C-19H), 1.75–1.85 (*m*,2H, C-12H), 3.65–3.68 (*brs*, methylene PEG protons on C-9 and C-10 carbons of the repeating units and on C-α and C-β), 3.78 (*t*, 2H, C-8H), 3.95 (*s*, 3H, -$COOCH_3$), 4.06 (*t*, 2H, C-11H), 4.51 (*t*, 2H, C-7H), 7.76 (*m*, 2H, C-4H and C-6H) and 8.31 (*s*, 1H, C-2H).

^{13}C-NMR Data ($CDCl_3$): δ 14.55 (C-20), 23.15–33.16 (C-12 to C-19), 52.89 (-OCH_3 end group), 61.75 (C-α), 64.85 (C-β), 69.48 (C-8 and C-11), 70.43–70.97 (repeating PEG units' carbons), 72.90 (C-7), 121.04 (C-4 and C-6), 123.53 (C-2), 132.0 (C-1 and C-3), 159.57 (C-5) and 166.11 (-COOMe).

2.3.4. *Poly[poly(oxyethylene-600)-oxy-5-(12-hydroxydodecanyloxy)-isophthaloyl]* **8a**

^{1}H-NMR Data ($CDCl_3$): δ 1.31 (*bs,* 3H, C-20H), 1.57–1.61 (*m*,C-2H to C-21H), 1.82 (*m*,2H, C-12H), 3.32–3.45 (*t*,2H, C-22H), 3.60–3.67 (*brs*, methylene PEG protons on C-9 and C-10 carbons of the repeating units and on C-α and C-β), 3.86 (*t*, 2H, C-8H), 3.95 (*s*, 3H, -$COOCH_3$end group), 4.05 (*t*, 2H, C-11H), 4.51 (*t*, 2H, C-7H), 7.76 (*m*, 2H, C-4H and C-6H) and 8.28 (*s*, 1H, C-2H).

^{13}C-NMR Data ($CDCl_3$): δ 26.16–33.18 (C-12-C-21), 52.89 (-OCH_3 end group), 61.82 (C-α), 63.25 (C-22), 64.87 (C-β), 69.48 (C-8 and C-11), 70.43–70.97 (repeating PEG units' carbons), 72.90 (C-7), 120.24 (C-4 and C-6), 123.53 (C-2), 132.04 (C-1 and C-3), 159.57 (C-5) and 166.11 (-COOMe).

2.4 Characterization

Static light scattering data was collected on a laser light scattering photometer (Wyatt Technology DAWN Model F) equipped with a 632 nm He-NE laser as the light source.

2.5 Sample Preparation

The solution of the amphiphilic copolymer, **7a–7d** and **8a–8d** were prepared by dispersing them in distilled water with gentle stirring for 30 min, followed by sonication for 15

min. The concentration of the samples were varied from 0.1 mg/ml to 100 mg/ml, the sample solutions were purified by passing through a Millipore 0.20 μm filter.

2.6 Encapsulation of Carbofuran in Nanoparticles

The amphiphilic polymers (**7a–7d**) (1.0 g) and carbofuran (0.100 g, 85% purity) were dissolved in dichloromethane separately and mixed together. This was then shaken well for 3 h and the solvent evaporated under vacuum. The residue was then dissolved in water and again shaken for 3 h. It was then filtered and the clear solution was freeze-dried to get the encapsulated material.

Carbofuran content was estimated using a Shimadzu high performance liquid chromatograph (HPLC) fitted with SPDM6A Photodiode array detector. Samples were resolved isocratically on a 15 cm × 3.9 mm id RP 18 column using acetonitrile-water (70:30) at 1 ml min^{-1} as mobile phase. The absorbance was recorded at 276 nm at sensitivity of 0.05 AUFS by injecting a volume of 20 μl. Recovery of carbofuran from different CR formulations varied from 94.2 to 99.5%.

2.7 Release of Carbofuran in Water

The release of carbofuran from the test controlled release formulations was determined as per literature with minor modifications (25,27). The term release has been taken to imply, as the amount of active ingredient recorded at a given time and has been taken as synonymous to release in this study for making different comparisons. An accurately weighed quantity of controlled release formulation and commercial granules containing about 6.0 mg of carbofuran for each sample (three replicates) in small capsules made from (5 × 5 cm^2) parchment strips was added to 25 ml water in a stoppered conical flasks. Flasks were kept in a BOD at 30± 1°C. At different time intervals (0, 1, 3, 7, 14, 21, 28, 35, 42, 49, 56 and 63 days), aliquots of 1 ml were removed for determination of carbofuran by HPLC, and then unused sample portions were returned to the flasks.

2.8 Analysis of the Release Data

2.8.1. *Determination of the diffusion exponents of the carbofuran in formulations*

The diffusion exponents from release data was calculated with the semi-empirical power law equation as suggested by Ritger and Peppas (32), Equation 1.

$$M_t/M_o = Kt^n \quad (1)$$

Where M_t/M_o is the fraction of active ingredient released at time t, K is a constant that incorporates characteristics (porosity) of the macro molecular network system and the active ingredients, and n, a diffusional parameter which is indicative of the transport mechanism. The model has been fitted by taking logarithm on both sides of Equation 1:

$$\log_e M_t/M_o = \log_e K + n \log_e t + e \quad (2)$$

The values of K and n were determined from carbofuran release.

2.8.2. *Calculation of $t_{1/2}$ (time taken for release of 50% of initial carbofuran).*

In most cases, the rate of removal of the pesticide follows first order kinetics. The rate of removal at a given time is directly proportional at the time. The first order rate law is given by flowing Equation 3:

$$dM/dt = -K_r M_t \quad (3)$$

Where, K_r = rate constant, dM /dt = rate of removal, M_t = amount of pesticide present at any time 't'.

The integrated solution to Equation 3 is:

$$\ln(M_t/M_\infty) = -K_t t \quad (4)$$

M_∞ is the amount incorporated in the matrix. The rate of removal of a pesticide from the environment is often expressed as agent's half-life $t_{1/2}$. The half-life is related to the first order rate constant for removal, K_r as follows:

$$\ln 2 = -K_r t_{1/2} \quad (5)$$

Or

$$K_r = (\ln 2/t_{1/2}) = (0.693/t_{1/2}) \quad (6)$$

2.9 Prediction of optimum availability (maximum feasible concentration) of carbofuran

The optimum availability of carbofuran from CR formulations was predicted by fitting the release data in the quadratic Equation 7.

$$AV_B = a + bt + ct^2 + e \quad (7)$$

Where as AV_B is available carbofuran, 'a' coefficient of initial concentration (t = 0); 'b' rate of change of concentration (t); 'c' product of rate of change and rate of change of concentration (t × t); and 'e' constant. Maximum feasible concentration is obtained from the expression –b/2c. To fit in to the equation, c has to be negative.The data were analyzed using SAS PROC NLIN and PROC REG of.

3 Results and Discussion

3.1 Particle Size Determination

The amphiphilic copolymers when dissolved in water above their critical micelle concentration (CMC) (Table 1), aggregate to form nano-micelles. The CMC values were determined by static light scattering and found independent on the size of hydrophilic segment PEG as no significant change in CMC values were observed in going from

Table 1. Critical micelle concentration and radius of gyration of copolymer **7a**–**7d** and **8a**–**8d**

Entry	*Nanospheres*	*Rg (nm)*	*CMC (mmol)*
1.	(IP - PEG)600 decane (**7a**)	17.85	3.17×10^{-5}
2.	(IP - PEG)900 decane (**7b**)	19.40	2.66×10^{-5}
3.	(IP - PEG)1500 decane (**7c**)	29.60	2.88×10^{-5}
4.	(IP - PEG)1800 decane (**7d**)	38.75	3.08×10^{-5}
5.	(IP - PEG)600 dodecanol(**8a**)	12.40	3.15×10^{-5}
6.	(IP - PEG)600 dodecanol (**8b**)	11.55	2.92×10^{-5}
7.	(IP - PEG)600 dodecanol (**8c**)	22.50	2.78×10^{-5}
8.	(IP - PEG)600 dodecanol (**8d**)	36.80	3.06×10^{-5}

PEG 600 to PEG 1800. However, the size of nano-micelles formed by the self assembly of copolymers **7a–7d** and **8a–8d** varied with hydrophilic segments. The radius of gyration (Rg) increased with the increase in the size of hydrophilic segment, (PEG size) and was found to be 17.85, 19.40, 29.60 and 38.75 nm for PEG 600, 900, 1500 and 1800, respectively with decane and 12.4, 11.5, 22.5 and 36.8 nm for PEG 600, 900, 1500 and 1800, respectively with 12-hydroxydodecanol (Table 1).

3.2 Release of Carbofuran from Test Formulations

Periodic release of carbofuran in water from the polymeric test formulations along with commercial formulation is depicted in Figure 1. The rate of release from controlled release (CR) formulations were much slower than the commercial 3G, which revealed its maximum release of active ingredient by 7th day, after which the a.i. content decreased, because of carbofuran degradation in water. In the case of test polymers such as:

Poly[Poly(Oxyethylene-600)-Oxy-5-Decanyloxyisophthaloyl] 7a,
Poly[Poly(Oxyethylene-900)-Oxy-5-Decanyloxyisophthaloyl] 7b,
Poly[Poly(Oxyethylene-1500)-Oxy-5-Decanyloxyisophthaloyl] 7c,
Poly[Poly(Oxyethylene-1800)-Oxy-5-Decanyloxyisophthaloyl] 7d,

The maximum concentration of a.i. was obtained between 21–49 days and after that the a.i. content decreased rapidly in water. Amphiphilic polymer, with PEG-600, based formulation released carbofuran faster, whereas that with PEG 1800, released it slower. In case of polymers with PEG-900 and 1500, the maximum release was observed on the 28th day and after that, the degradation was faster. At the 63rd day, a detectable level of a.i. was present in all the above formulations. It appears that due to the complete release of carbofuran from CR formulation, its faster degradation occurred between 28–63 days. The non-biodegradable, hydrophobic polymer with crosslinked matrices such as polyvinyl chloride, showed slower release (Figure 1). The concentration of a.i. increased slowly to a maximum of its possible release between 49–63 days. In the case of polyvinyl chloride, maximum released was obtained on the 63rd day and showed the slowest release. So long as carbofuran was retained in a stable polymeric structure, it was protected from biotic and abiotic losses. In case of commercial 3G, carbofuran was detectable up to 28 days, whereas all polymeric formulations, it was detectable up to 63 days. The a.i. was present in a higher concentration at 63 days, also in synthetic CR formulations. Linear release was evident in all the formulations up to their maximum release level. Similar results were obtained for the release of phorate from polyvinyl chloride, polystyrene and polyethylene glycol 6000 matrices, (27) diuron from granules based on lignin matrix (28–29) and from an alginate-bentonite formulation (30–31). The values of K and n obtained from carbofuran released in water are presented in Table 2. There is a good correlation of the release of carbofuran from the CR formulations with time up to the increasing release level. When the cumulative release decreased, this equation did not provide a significant correlation with release. The

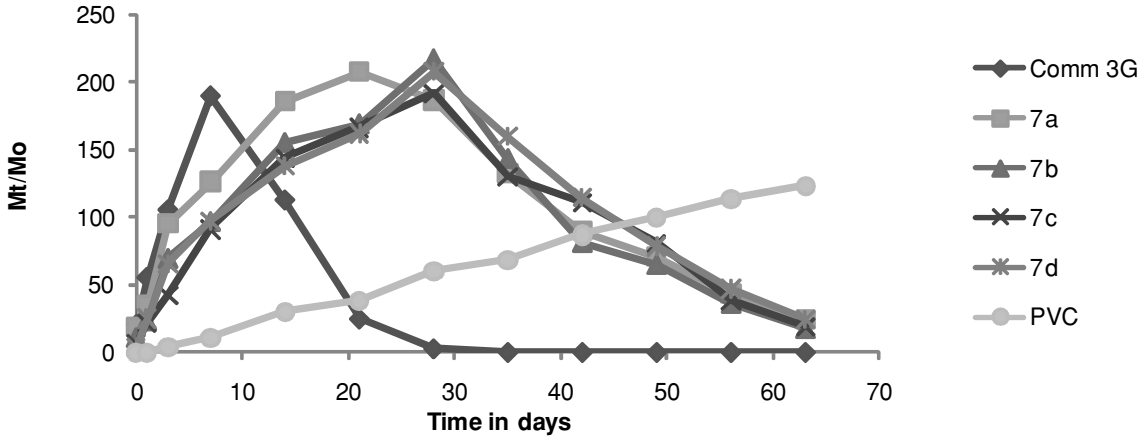


Figure 1. Release of carbofuran in water from controlled release formulations.

Table 2. The constants derived from fitting of the empirical equation $M_t / M_o = Kt^n$ to release data of carbofuran in water from controlled release and commercial formulations

Formulation	*ln (K)*	*SE*	*n*	*SE*	R^2	*SE*	$t_{1/2}$ *(days)*
Commercial 3G	1.45	0.029	0.62	0.024	0.99	0.001	3.2
Poly[Poly(Oxyethylene-600)-Oxy-5-Decanyloxyisophthaloyl] **7a**	1.81	0.032	0.59	0.012	0.96	0.001	7.5
Poly[Poly(Oxyethylene-900)-Oxy-5-Decanyloxyisophthaloyl] **7b**	2.19	0.031	0.64	0.013	0.97	0.003	9.2
Poly[Poly(Oxyethylene-1500)-Oxy-5-Decanyloxyisophthaloyl] **7c**	2.42	0.041	0.69	0.021	0.99	0.003	12.2
Poly[Poly(Oxyethylene-1800)-Oxy-5-Decanyloxyisophthaloyl] **7d**	2.10	0.018	0.59	0.015	0.98	0.002	11.1
Polyvinyl chloride	4.93	0.024	1.05	0.024	0.99	0.004	55.0

n value ranged from 0.5400 to 1.1116 for controlled release formulation and commercial formulation. Values close to 0.5 are stated to indicate that the release is diffusion controlled (23). The difference in n values may be due to the different chemical nature of the polymers.

The half life ($t_{1/2}$; time taken for the 50% release) of carbofuran in water from controlled release and commercial formulations is reported in Table 2. The $t_{1/2}$of carbofuran in commercial 3G formulation was found 3.2 days. The release of carbofuran followed first order kinetics. The $t_{1/2}$ value of different controlled release formulations ranged from 7.5 to 60.3 days in water. In order of increasing $t_{1/2}$ values, the various formulations revealed the following order:

Poly[Poly(Oxyethylene-600)-Oxy-5-Decanyloxyisophthaloyl] 7a < Poly[Poly(Oxyethylene-900)-Oxy-5-Decanyloxyisophthaloyl] 7b < Poly[Poly(Oxyethylene-1500)-Oxy-5-Decanyloxyisophthaloyl] 7c < Poly[Poly(Oxyethylene-1800)-Oxy-5-Decanyloxyisophthaloyl] 7d < PVC.

The value of $t_{1/2}$ of carbofuran in various test polymers such as **7a-7d** was less than 12.2 days and for non-biodegradable polymer such as PVC, were more than 44 days in water, implying very slow release.

Amongst the various developed controlled release formulations, the polymer, obtained after derivatization of amphiphilic copolymer, **4a**, with bromodecane, showed minimum value of $t_{1/2}$ (days) whereas PVC has shown maximum $t_{1/2}$ (days). The lowest of value of $t_{1/2}$ implied faster carbofuran release in water. It appears that by increasing the molecular weight of PEGs during polymerization, the rate of release of toxicant from nanosphere in water is reduced.

The period of optimum availability (POA) of carbofuran in water from test formulations by fitting the release data in quadratic equation ($POA = a + bx + cx^2 + e$) is reported in Table 3. It ranged from 8.97 to 67.53 days. The period of optimum availability of carbofuran in water was found in following order:

Commercial 3G < **7a** < **7b** < **7c** < **7d** < PVC

4 Conclusions

The encapsulation of carbofuran in nano micelles, formed by the self assembly of copolymers, was achieved. The results suggest that depending on the matrix of the polymer used, the carbofuran applications can be optimized to achieve insect control for the desired period. Single application of the formulation can be manipulated for insect/nematode control during the whole growth span of the crop. The $T_{1/2}$ values and the period of optimum availability will be useful in preparing the most appropriate formulation for use in a given situation.

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Table 3. Prediction of period of optimum availability (POA) of carbofuran in water from controlled release formulations in water by fitting the release data in quadratic equation ($AV_B = a + bx + cx2 + e$)

Formulation	*Intercept*	R^2	*Prob.>F*	*POA (days)*
Commercial 3G	0.076	0.98	0.066	8.97
Poly[Poly(Oxyethylene-600)-Oxy-5-decanyloxyisophthaloyl] **7a**	0.124	0.96	0.063	20.25
Poly[Poly(Oxyethylene-900)-Oxy-5-Decanyloxyisophthaloyl] **7b**	0.142	0.79	0.039	29.43
Poly[Poly(Oxyethylene-1500)-Oxy-5-Decanyloxyisophthaloyl] **7c**	0.086	0.88	0.045	29.73
Poly[Poly(Oxyethylene-1800)-Oxy-5-Decanyloxyisophthaloyl] **7d**	0.063	0.97	0.035	28.47
Polyvinyl chloride	−0.011	0.99	0.084	66.50

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