Synthesis of Polyacrylamides from Derivatives 2-Aminobenzothiazole and also Preparation of Dibutylphthalate as a Plasticizer to Estimate Plasticization Behaviour for Prepared Polymers

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Abstract

The present research involved preparation of heterocyclic polyacrylamides using reaction of polyacryloyl chloride with 2-aminobenzothiazole in the presence of a suitable solvent and amount of triethyl amine with heating. After that, Dibutylphthalate (DBP) has been used as a plasticizer for some prepared polymers, this plasticizer has shown a good behaviour toward change of softening point for these polymers, the optimal weight of DBP that must be added to polymer has been estimated by plotting between softening points of polymers with weight of DBP that added to polymers, the method used in this research can be applied to other polymers and other plasticizers to find optimal weight of plasticizer that give minimum softening points.

Keywords: Derivatives of polyacrylamides, dibutylphthalate, plasticizer.

Introduction

Polyacrylamide is a polymer (-$CH_2CHCONH_2$-) formed from acrylamide subunit. It can be synthesised as a simple linear-chain structure or cross-linked, typically using N, N-methyllenebisacrylamide. Polyacrylamide is not toxic, however, unpolymerized acrylamide, which is a neurotoxin, can be present in very small amounts in the polymerized acrylamide, [1,2] therefore, it is recommended to handle it with caution. In cross-linked form, the possibility of the monomer being present is reduced even further. It is highly water-absorbent, forming a soft gel when hydrated, used in such applications as polyacrylamide gel electrophoresis and in manufacturing soft contact lenses. Another common use of poly acrylamide and its derivatives are in subsurface applications such as enhanced oil recovery. [3,4] Polyacrylamide is often used as a medium for electrophoresis of proteins and nucleic acids in a technique known as PAGE.[4]

Plasticizers are an important class of low molecular weight and non volatile compounds that are widely used in polymer industries as additives. [5-7] The primary role of such substances is to improve the flexibility and process ability of polymers by lowering the second order transition temperature. [8-11] These substances reduce the tension of deformation, hardness, density, viscosity and electrostatic charge of a polymer, at the same time as increasing the polymer chain flexibility, resistance to fracture and dielectric constant. [12-16]

Phthalates are a group of synthetic chemicals with widespread use in the industrial production of numerous products.[17] They are used to soften plastics found in numerous flexible plastics products and personal care products such as food packing and food-contact materials, cosmetics, toys, bags, drugs and building material. [18-20] During the last thirty years, numerous studies have been published concerining. [21]

DBP is a phthalate diester that is used mainly as a plasticizer for nitrocellulose, polyvinyl acetate, and polyvinyl chloride, a lubricant, an antifoaming agent, and skin emollient. [22-25] Indeed DBP, the main kind of plasticizers used in China at present, is one of the main sources of indoor semi volatile organic compounds (SVOCs). [26] In this contribution the polyacrylamides were prepared by condensation poly acryloylachloride (PAC) with 2-aminobenzothiazole. In order to study the plastization behaviour of polyacrylamides, Dibutylphthalate (DBP) was prepared and used as a plasticizer for some prepared polymers.

1. Experimental Section

1. Softening points were determined using thermal microscope (Kofler-method). Reichert thermovar. SP. 10/0.25, 160, College of Science at Baghdad University,
2. All chemicals used were of the highest purity available. Employed chemicals were supplied from Fluka and BDH.
3. FT-IR spectra were recorded using solid KBr discs by testing Schimadzu FT-IR 8000 series fourier transform infrared spectrophotometer, Ministry of Industry and materials, Ibn Sina State company.
4. ^{1}HNMR spectra were recorded on a fourier transform varian spectrometry, company Burkur, model, Ultra shield 300 MHz, origin: Switzerland, with tetramethyl silane as internal standard in DMSO, measurements were made at the chemistry Department, Ahl-Albyt University, Jordan.

1.1 General Procedure Preparation of poly 2-(N-acryl-N-sub. Or un sub. acetyl of benzoyl) Imidyl Substituted Benzothiazole. [27]

A mixture of poly (acryloyl chloride) (0.06 mol), (0.06 mol) of 2-N-sub amidyl-sub benzothiazol, (1 ml) of triethyl amine Et_3N and (25 ml) of a suitable solvent (DMSO or DMF) was heated under refluxing for (5-7) hrs. The solid was separated and purified by dissolving at DMF or DMSO and reprecipitating from water or acetone. All physical properties of prepared polyacrylamides were listed in Table(1).

1.2 Preparation of dibutylphthalate [23]

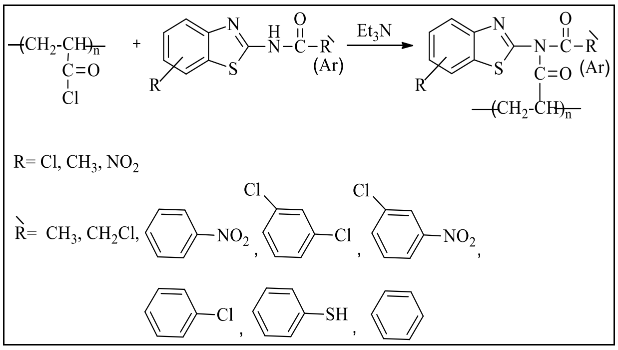
A mixture of (1.5) gm phthalic anhydride and dissolved in a mixture of (18.2) ml of n-butanol and (25) ml of benzene was heated under refluxing for 3 hrs. The oily product of dibutyl phthalate has been cooled and kept at room temperature.

1.3 Addition of plasticizer to polymers

In a round bottom flask, (3 ml) of dibutylphthalate was placed at 130-140˚C with stirring. Then (0.5 gm) of polymers (1-10) were added gradually to the hot dibutylpthalate until homogeneity. Finally, the hot mixture was cooled to producing of solid polymer. Physical properties of polymers (1-10) after addition of plasticizer are shown in table -2.

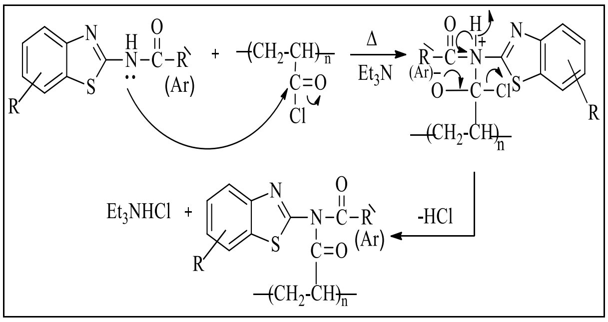
2. Results and Discussion

New polymers were prepared by the reaction of poly (acryloyl chloride) with different amides in the presence of triethyl amine (Et_3N) as a catalyst.[26, 27] As shown below in scheme (1):



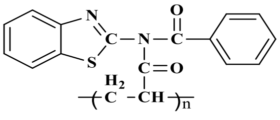
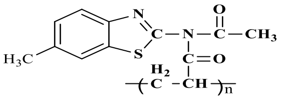
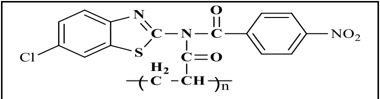
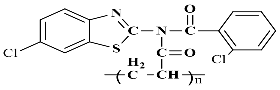
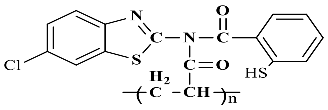
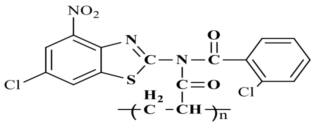
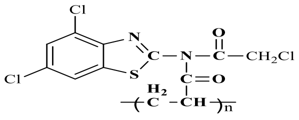
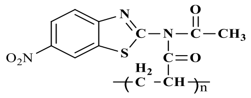
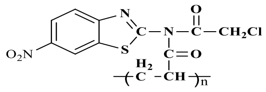
Scheme (1) Preparation of poly 2-[N-acryl-N-(sub.aryl or acetyl)imidyl substituted benzothiazole.

The mechanism of the reaction involves a nucleophilic attack on the carbonyl [26, 27] as shown below in scheme (2):



Scheme (2) ***Mechanism of preparation of poly 2-[N-acryl-N-(sub.aryl or acetyl) imidyl substituted benzothiazole.***

Table (1)
Physical properties of the prepared poly imides.

Comp. No.	***Structure***	***Conversion %***	***Softening Point ˚C***	***Colour***	***Solubility of polymer***
1	 Poly 2-[N-acryl)-N-benzoyl] imidyl benzothiazole	80	180-195	Brownish yellow	DMSO
2	 Poly2-[N-acryl)-N-acetyl]imidyl-6-methyl benzothiazole	87	130-140	light yellow	DMF
3	 Poly 2-[N-acryl)-N-acetyll] imidyl benzothiazole	80	130-145	yellow	DMF
4	 Poly2-[N-acryl)-N-(2-chlorobenzoyl)]imidyl-6-chloro benzothiazole	80	210-225	yellow	DMSO
5	 Poly2-[N-acryl)-N-(2-mercaptoenzoyl)]iimidyl-6-chloro benzothiazole	82	130-140	Light yellow	DMF
7	 Poly2-[N-acryl)-N-(2-chlorobenzoyl)]imidyl-6-chloro-4-nitro benzothiazole	82	165-175	Brownish yellow	DMSO
8	 Poly2-[N-acryl)-N-(chloroacetoyl)]imidyl-4,6-dichloro benzothiazole	70	170-180	Light yellow	DMF
9	 Poly2-[N-acryl-N-acetyl]imidyl-6-nitro benzothiazole	84	190-202	Light yellow	DMSO
10	 Poly2-[N-acryl-N-(chloroacetoyl] imidyl- 6-nitro benzothiazole	84	210-220	brown	DMF

Structures of all prepared polymers in this work were confirmed using FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. Physical properties including softening point, solubility (the polymers soluble in DMSO and DMF only) and percent conversion of the polymers were also measured. These and other physical properties are summarised in Table (1). In general the FT-IR spectra of compounds 1-10 in KBr disk showed the following characteristic features: stretching bands at (1780-1785) cm^{-1} due to carbonyl (C=O) for imide which revealed a good indication for formation of the imide. Another general new band appeared in all the spectra of the polymers containing imides which belong to (C-N) stretching vibration at (1340-1365)cm^{-1}. The weaker (C-H) stretching bands were appeared at 2900-2978 cm^{-1} .due to (C-H, CH_2, CH_3) aliphatic groups, another characteristic absorption bands was appeared at 1550 cm^{-1} , 667 cm^{-1} , 3074 cm^{-1}, 779 cm^{-1} due to ν (C=C) aromatic, ν (C-S), ν (C-H) aromatic and ν (C=S) thiazole ring respectively.

As well as, the FT-IR spectra of compounds [3,7,9,10] showed the same bands in compound 1 except ν ($C-NO_2$) due to nitro group shown at 1340-1365 cm^{-1} and ν (C-Cl) at 1037-1157 cm^{-1}. These bands and other FT-IR absorption bands are listed in Table (3).

^{1}H-NMR spectra of compound [2], [9], [10] showed characteristics signals belongs to these compounds as shown in Table (3) and Figures (1-3). A polymer [9] showed signals singlet at δ (2.6) ppm, triplet at δ (1.08) ppm, multiplate at δ (3.4) and doublet at δ (7-8) ppm belong to (CH_3), (CH_2) to $-(C\underline{H_2}-CH)-_n$ and (CH) to $-(CH_2-C\underline{H})-_n$ and aromatic protons respectively. While ^{13}C-NMR spectrum of this compound showed signals at δ (44) ppm, δ (120-140) ppm belong to (CH_2), aromatic carbons respectively as shown in Table (4) and Fig.(4).

Also a polymer [10] showed signals at δ (3) ppm, triplet at δ (1.03) ppm, multiplate at δ (3.5) ppm and doublet at δ (7-8) ppm belong to CH_2Cl, (CH_2) to $-(C\underline{H_2}-CH)-_n$, (CH) to $-(CH_2-C\underline{H})-_n$ and aromatic protons respectively. These signals and others are listed in Table(3).

As mentioned above in experimental section that plasticizer DBP was added to prepared polymers [1-10] and measured softening point for each one. This plasticizer is suitable for these polymers and it can be used to increase plasticization characteristic for them.

There are an agreement among the polymers, which they are [2-5] in their behaviour when the DBP added to them, all these polymers having minimum softening point when 0.5 gm of DBP added to them, after this amount of DBP (when the weight of DBP is more than 0.5 gm) the softening point will increase again. So the optimal weight that must be added to polymers [2-5] is 0.5 gm.

Structures of polymers that used and tested in this experiment with some physical properties have listed in Table (2). As that shown in Table (2) the softening of polymers [1-5] before addition of DBP is higher than these recorded after addition of DBP, the softening points have sharply declined after addition.

Table (2)
Structures of polymers and some physical properties with experimental details after addition.

Comp. No.	*Wt of polymer (gm)*	*Wt. of DBP (gm)*	*Softening point with DBP*	*Softening point without DBP*
1	0.5	0.1	80-92	180-195
	0.5	0.2	50-60	
	0.5	0.5	55-66	
	0.5	1	69-78	
2	0.5	0.1	82-92	130-140
	0.5	0.2	54-64	
	0.5	0.5	49-59	
	0.5	1	55-65	
3	0.5	0.1	60-70	130-145
	0.5	0.2	58-65	
	0.5	0.5	44-55	
	0.5	1	54-62	
4	0.5	0.1	75-82	120-135
	0.5	0.2	64-51	
	0.5	0.5	49-55	
	0.5	1	54-66	
5	0.5	0.1	85-93	140-165
	0.5	0.2	59-67	
	0.5	0.5	44-67	
	0.5	1	44-58	
6	0.5	0.1	101-110	190-200
	0.5	0.2	72-80	
	0.5	0.5	52-61	
	0.5	1	41-50	
7	0.5	0.1	81-90	165-175
	0.5	0.2	62-75	
	0.5	0.5	53-60	
	0.5	1	40-51	
8	0.5	0.1	86-95	170-180
	0.5	0.2	69-80	
	0.5	0.5	56-65	
	0.5	1	42-50	
9	0.5	0.1	94-105	190-202
	0.5	0.2	71-85	
	0.5	0.5	59-70	
	0.5	1.0	44-54	
10	0.5	0.1	119-130	210-220
	0.5	0.2	94-105	
	0.5	0.5	71-83	
	0.5	1	54-65	

Table (3)
FT-IR data of prepared poly imides cm^{-1}.

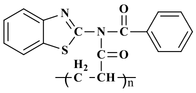
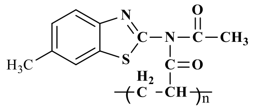
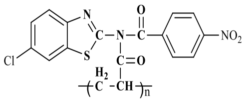
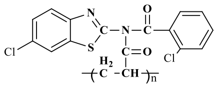
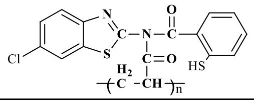
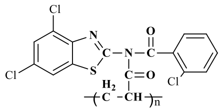
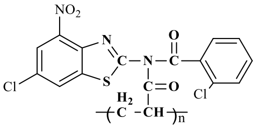
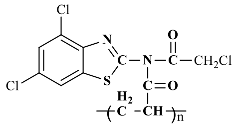
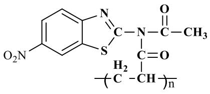
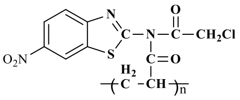
Comp. No.	*Structure*	*v(C=O) imide*	*v(CN)*	*v(C=N) imine*	*v(CH) aliphatic*	*v(CH) aromatic*	*v(C=C) aromatic*	*v(C=S)*	*Other bands*
1		1690	1420	1610	2975 2905	3000	1520	700	-
2		1693	1400	1600	2978 2943	3132	1550	667	-
3		1697	1444	1600	2975 2939	3010	1548	684	(C-Cl) 1035 (C-NO_2) 1365
4		1697	1446	1666	2974 2943	3062	1550	767	(C-Cl) 1099
5		1674	1473	1604	2978 2934	3062	1535	763	(C-Cl) 1037
6		1681	1442	1585	2950 2900	3100	1539	610	(C-Cl) 1034
7		1708	1400	1543	2978 2943	3100	1543	750	(C-Cl) 1037 (C-NO_2) 1346
8		1716	1431	1635	2975 2947	3074	1535	779	(C-Cl) 1157
9		1698	1400	1589	2940 2920	3070	1500	610	(C-NO_2) 1365
10		1690	1410	1602	2990	3030	1500	620	(C-NO_2) 1340

Table (4)
The ^{1}H-NMR chemical shifts of some prepared poly imides.

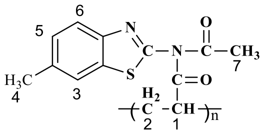
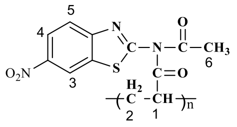
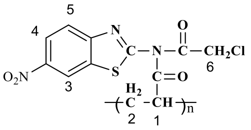
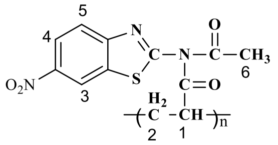
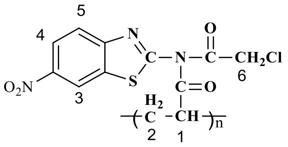
Comp. No.	Structure	Chemical shifts in ppm	Fig. No.
2		δ 1.03 (s, 3H^7, CH$_3$); δ 3.0-3.5 [t, 2H^2, (-($\underline{\mathrm{H_2}}$C-CH-)n]; δ 4.2 [m, 1H^1, (-(H$_2$C-C$\underline{\mathrm{H}}$-)n]; δ 3.0 (s, 3H^4, CH$_3$) δ 7.0-8.2 (d, H^5, H^6, HAr). δ 8.2 (s,H^3, HAr)	1
9		δ 1.08 [t, 2H^2, (-($\underline{\mathrm{H_2}}$C-CH-)n]; δ 2.6 (s, 3H^6, CH$_3$); δ 3.4 [m, 1H^1, (-(H$_2$C-C$\underline{\mathrm{H}}$-)n]; δ 7.0-8.0 (d, H^4, H^5, HAr); δ 8.4 (s, 1H^3,HAr).	2
10		δ 1.03 [t, 2H^2, (-($\underline{\mathrm{H_2}}$C-CH-)n]; δ 3.0 (s, 2H^6, CH$_2$Cl); δ 3.5 [m, 1H^1, (-(H$_2$C-C$\underline{\mathrm{H}}$-)n]; δ 7.0-8.0 (d, H^4, H$_5$, HAr); δ 8.5 (s, 1H^3,HAr).	3

Table (5)
The ^{13}C-NMR chemical shifts of some prepared polyimides.

Comp. No.	Structure	Chemical shifts in ppm	Fig. No.
9		δ 44 (-(H$_2\underline{\mathrm{C}}$-CH-)n]; δ 128 (C5); δ 140 (C3, C4). δ 157 ($\underline{\mathrm{C}}$=N).	4, 5
10		δ 46 (-(H$_2\underline{\mathrm{C}}$-CH-)n]; δ 120-128 (C3, C4); δ 140 (C3, C4). δ 145 ($\underline{\mathrm{C}}$-NO$_2$). δ 159 ($\underline{\mathrm{C}}$=N).	6

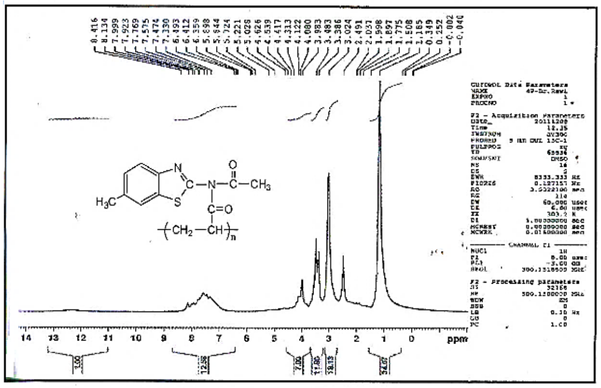


Fig.(1): ^{1}H-NMR of compound [2].

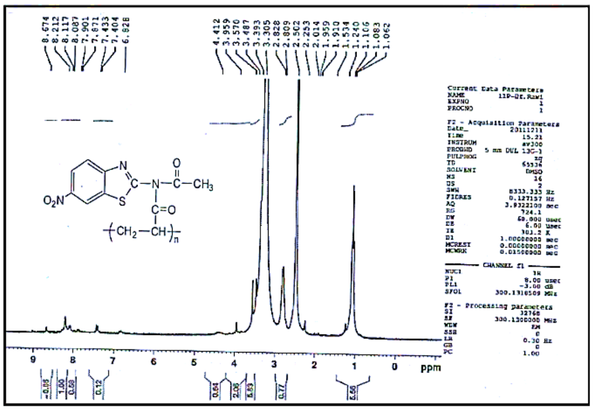


Fig.(2): ^{1}H-NMR of compound [9].

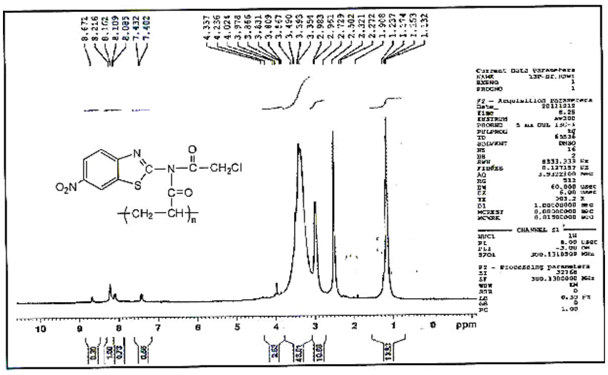


Fig.(3): ^{1}H-NMR of compound [10].

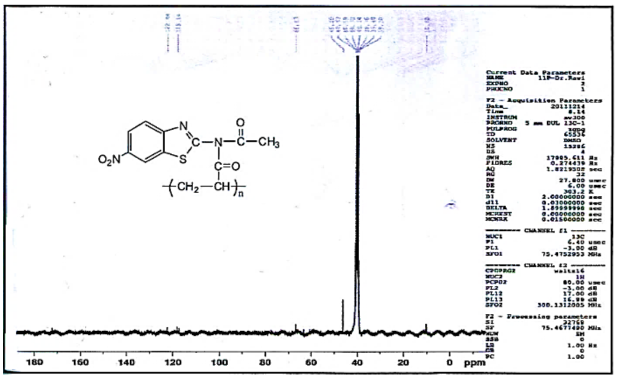


Fig.(4): ^{13}C-NMR of compound [9].

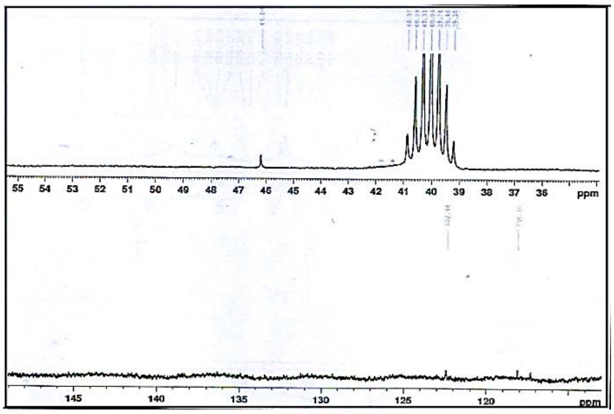


Fig.(5): The expansion of ^{13}C-NMR of compound [9].

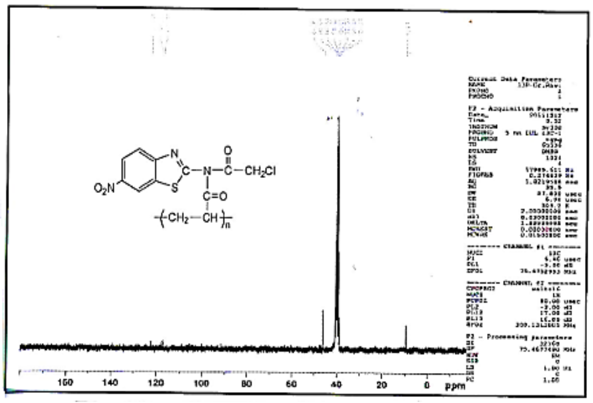


Fig.(6): ^{13}C-NMR of compound [10].

References

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الخلاصة

في هذا البحث تم تحضير بولي اكريل امايدات من 2− امينو بنزوثايازول وكذلك تم استخدام داي بيوتيل فثاليت كملدن لبعض البوليمرات المحضرة حيث اظهر هذا الملدن تصرف جيد بزيادة درجة التليين لبعض البوليمرات وقد تم تخميين الوزن المثالي للملدن والذي يجب اضافته لهذه البوليمرات بواسطة رسم بياني بين درجة التليين ووزن الملدن (داي بيوتيل فثاليت) وهذه الطريقة يمكن تطبيقها على بوليمرات وملدنات اخرى لايجاد الوزن المثالي للملدن والذي يعطي درجة تليين مناسبة وكاستنتاج نهائي يمكن استخدام داي بيوتيل فثالييت لتليين المواد البلاستيكية الموجودة في العديد من المنتجات المرنة.